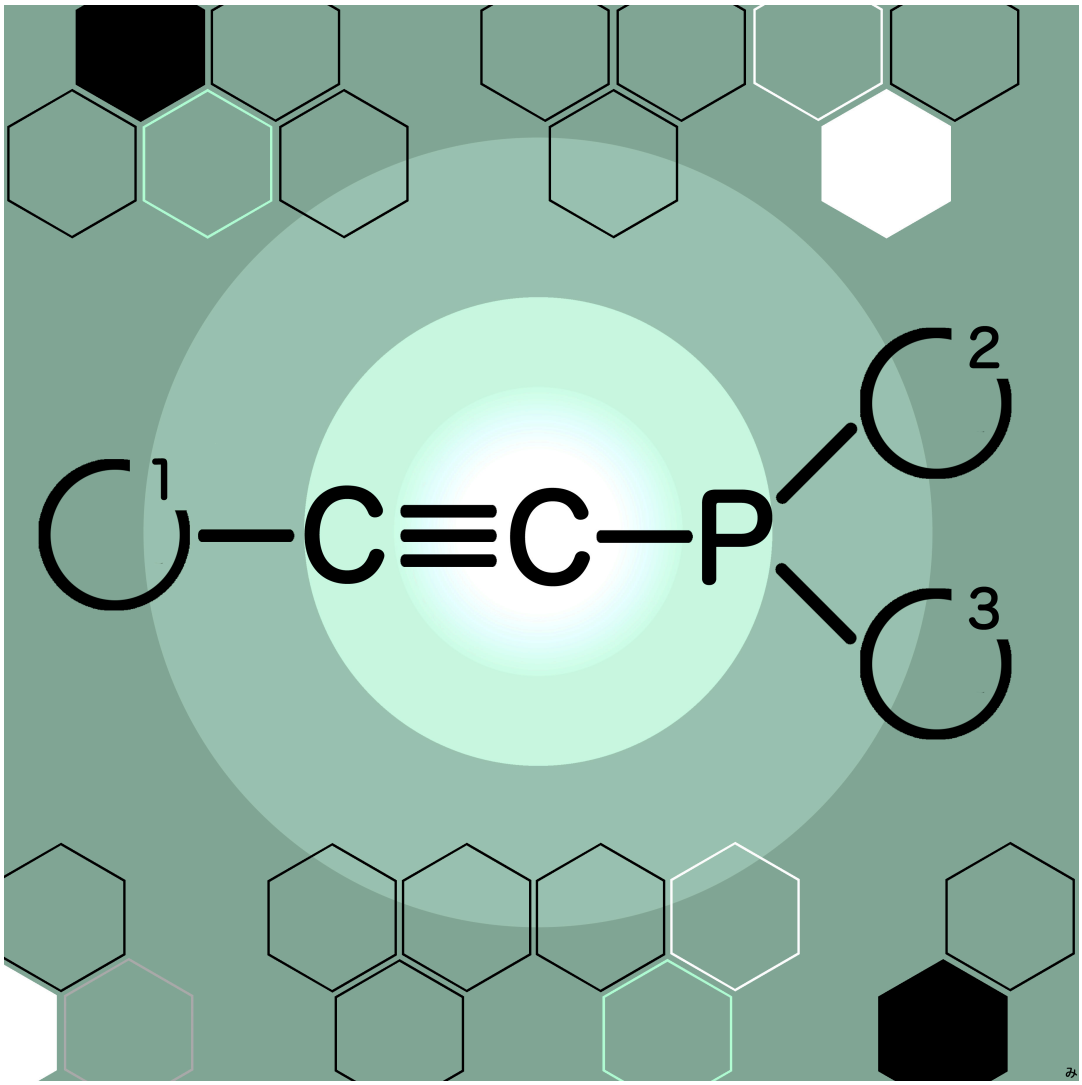
Studies on 1-Alkynylphosphines and Their Derivatives as Key Starting Materials in Creating New Phosphines



Azusa Kondoh

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Contents

α	observed optical rotation (in degrees)
Ac	acetyl
acac	acetylacetonate
AIBN	2,2'-azobis(isobutyronitrile)
Am	amyl
aq.	aqueous
Ar	aryl
atm	atmosphere
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	1,1'-bi-2-naphthol
BIPHEP	2,2'-bis(diphenylphosphino)biphenyl
Bn	benzyl
Boc	*tert*-butoxycarbonyl
bp	boiling point
br	broad (spectral)
Bu	butyl
c	cyclo, concentration
°C	degrees Celsius
ca.	*circa* (about)
calcd	calculated
cat.	catalytic
cm	centimeter(s)
Co.	company
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
δ	chemical shift in parts per million downfield from tetramethylsilane
d	doublet (spectral)
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIAD	diisopropyl azodicarboxylate
DMA	*N*,*N*-dimethylacetamide
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
DPPE (dppe)	1,2-bis(diphenylphosphino)ethane
DPPF	1,1'-bis(diphenylphosphino)ferrocene
Ed(s).	editor(s)
ee	enantiomeric excess
EI	electron impact
eq	equation
equiv	equivalent(s)
Et	ethyl
FAB	fast atom bombardment
g	gram(s)
gem	geminal
h	hour(s)
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrometry
Hz	hertz (s^{-1})
i	iso
i.e.	that is
IR	infrared (spectrum)
J	coupling constant (spectral)
m	multiplet (spectral), meter(s), milli
m	meta
M	molar (1 M = 1 mol dm^{-3})
M^+	parent molecular ion
Me	methyl
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
mmol	millimole
m.p.	melting point
m/*z*	mass-to-charge ratio
n	normal
NMP	1-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
Np	naphthyl
o	ortho
p	para
p. (pp.)	page(s)
Ph	phenyl
ppm	parts per million (spectral)
Pr	propyl
q	quartet (spectral)
quant.	quantitative
ref(s)	reference(s)

R^L	larger group
R^S	smaller group
rt	room temperature (25 ± 3 ˚C)
s	singlet (spectral)
sept	septet (spectral)
t	triplet (spectral)
t (*tert*)	tertiary
temp.	temperature
THF	tetrahydrofuran
TLC	thin-layer chromatography
Tf	trifluoromethanesulfonyl
tfa	trifluoroacetate
TMEDA	*N*,*N*,*N'*,*N'*-tetramethylethylenediamine
TMS	trimethylsilyl
Ts	*p*-toluenesulfonyl
TTMSS	tris(trimethylsilyl)silane
vide infra	see below
vide supra	see above
Vol(s).	volume(s)

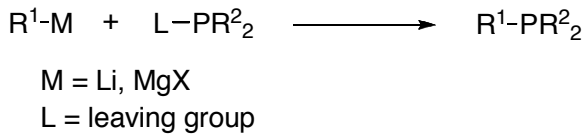
General Introduction

1. Introduction

Organophosphines play invaluable roles in organic synthesis, especially as ligands for transition metal catalysts. A variety of phosphine ligands have been designed and used in many reactions including cross-coupling reactions[1] and asymmetric transformations[2]. Creation of new organophosphines and development of novel approaches to organophosphines are thus quite important.

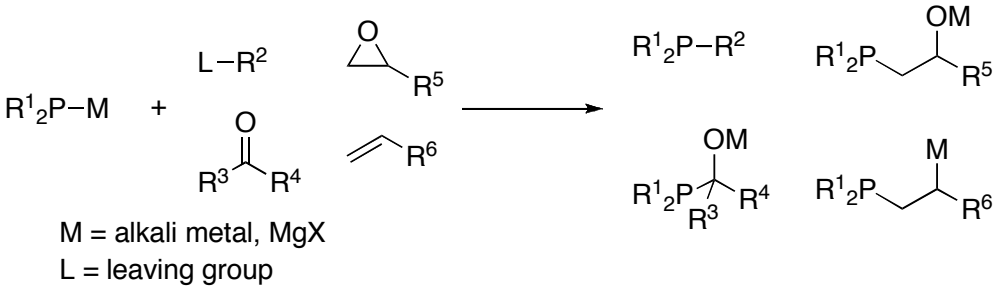
There are some general methods for the synthesis of phosphines. One of the most general methods is a reaction of an organometallic reagent such as an organolithium reagent or a Grignard reagent with a halophosphine or any phosphines with a good leaving group (Scheme 1).

Scheme 1.

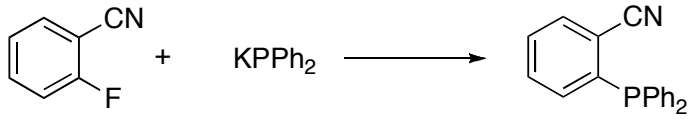


Another method is a reaction of a metal phosphide with an organic electrophile. Metal phosphides can be prepared by metalation of hydrophosphines by strong bases such as butyllithium or alkali metals. Halophosphines can be also metalated by using lithium metal. These nucleophilic reagents react with common electrophiles such as organohalides, tosylates, aldehydes, ketones, epoxides, and activated alkenes (Scheme 2). Phosphide reagents also react with activated arenes to afford mixed arylphosphines (Scheme 3).

Scheme 2.

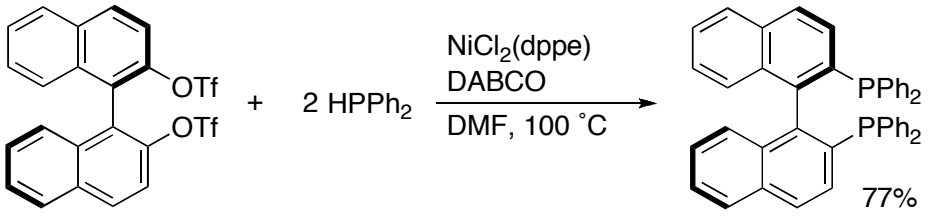


Scheme 3.



The other important method for the synthesis of phosphines utilizes transition metal catalysts. A transition-metal-catalyzed approach often enables the incorporation of sensitive functional groups into the target phosphine. One example is shown in Scheme 4. The synthesis of chiral BINAP was achieved using nickel-catalyzed cross-coupling of 2,2'-naphthol-derived ditriflate with diphenylphosphine.[3] Not only nickel complexes but also palladium[4] and copper complexes[5] can catalyze the cross-coupling of aryl halides or aryl triflates with secondary phosphines to provide tertiary arylphosphines.

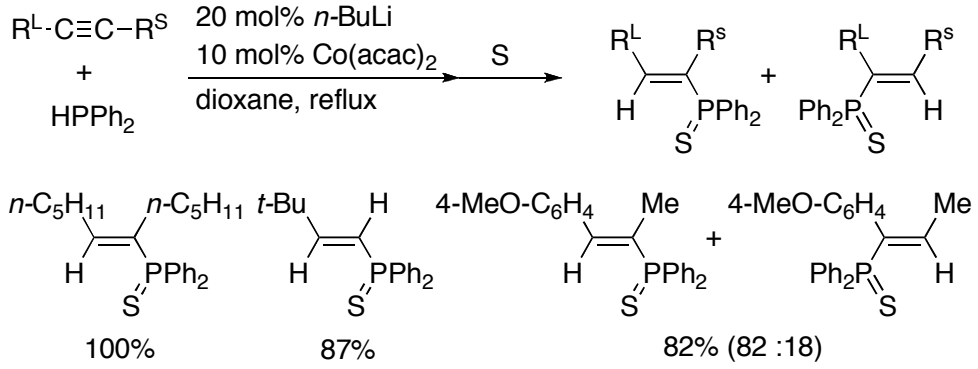
Scheme 4.



Besides the cross-coupling reaction, transition metal catalysts are also utilized for hydrophosphination of unsaturated substrates. The reaction of P–H bonds with unsaturated substrates often proceeds without a metal catalyst. In addition, acid- or base-catalyzed as well as radical reactions have been developed. However, transition-metal-catalyzed transformation,

often offers improvements in rate, selectivity, and stereocontrol. For instance, Oshima and co-workers reported cobalt-catalyzed *syn*-hydrophosphination of alkynes to provide (*E*)-alkenylphosphines, which is complementary to *anti*-selective radical hydrophosphination reactions (Scheme 5).[6]

Scheme 5.



1-Alkynylphosphines and Their Derivatives

1-Alkynylphosphines are an attractive and useful class of phosphines[7] in the field of coordination chemistry because of their versatile behavior, which results from their ability to react at the phosphine and the alkyne functions. 1-Alkynylphosphines can coordinate to metal centers via phosphorus atom and/or alkyne moiety, thus favoring the formation of a rich variety of homo- or heteropolynuclear species.[8] They also have an aptitude to act as sources of phosphido and alkynyl fragments via metal-mediated P–C bond cleavage.[9] The studies on a broad range of 1-alkynylphosphine–metal complexes have revealed other interesting abilities of these phosphines. For instance, the 1-alkynylphosphines in bis(1-alkynylphosphine)platinum undergo dimerization on the platinum, reacting at the two alkyne moieties to yield a bidentate phosphine–platinum complex.[10] The triple bonds of 1-alkynylphosphines are reactive enough to undergo insertion into some M–H and M–C bonds to form new transition metal complexes.[11] In addition, 1-alkynylphosphines serve as useful ligands in some transition-metal-catalyzed reactions.[12]

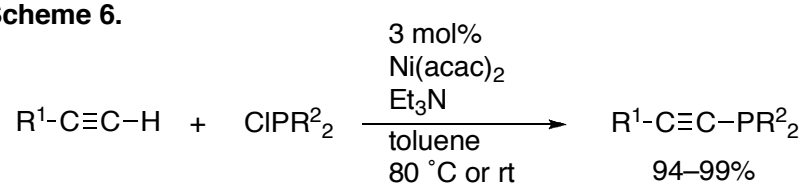
Meanwhile, 1-alkynylphosphines and their derivatives, such as phosphine oxides and phosphine sulfides, can be identified as useful building blocks in constructing other phosphines. For example, nucleophilic additions to a carbon–carbon triple bond lead to the formation of functionalized alkenylphosphines. Cycloadditions with other unsaturated bonds lead to the construction of cyclic structures having phosphorus pendants. The following are preparation of 1-alkynylphosphines and their derivatives, and representative reactions in which 1-alkynylphosphines and their derivatives are used as key starting materials.

1.1. Preparation of 1-Alkynylphosphines and Their Derivatives

Synthesis of 1-alkynylphosphines is usually accomplished by nucleophilic substitution reactions of halophosphines with acetylides of sodium,[13a] lithium,[13a] magnesium,[13b] or titanium.[13c]

An alternative approach to 1-alkynylphosphines is transition-metal-catalyzed coupling reactions of terminal alkynes with chlorophosphines.[14,15] Treatment of terminal alkynes with chlorophosphines in the presence of a nickel catalyst affords 1-alkynylphosphines in good yields (Scheme 6).[14] Besides the nickel complex, palladium[14] and copper complexes[15] also catalyze the coupling of terminal alkynes with chlorophosphines.

Scheme 6.



R^1 = Ph, 4-Me-C_6H_4, *n*-Pr, Am, *t*-Bu
R^2 = Ph, *i*-Pr, *n*-Bu

1-Alkynylphosphine oxides can be usually synthesized by the oxidation of the corresponding 1-alkynylphosphines. 1-Alkynylphosphine sulfides can be obtained by treatment of the corresponding 1-alkynylphosphines with crystalline sulfur.

1.2. Nucleophilic Addition to 1-Alkynylphosphines and Their Derivatives

1.2.1. Addition of Heteroatom Nucleophiles

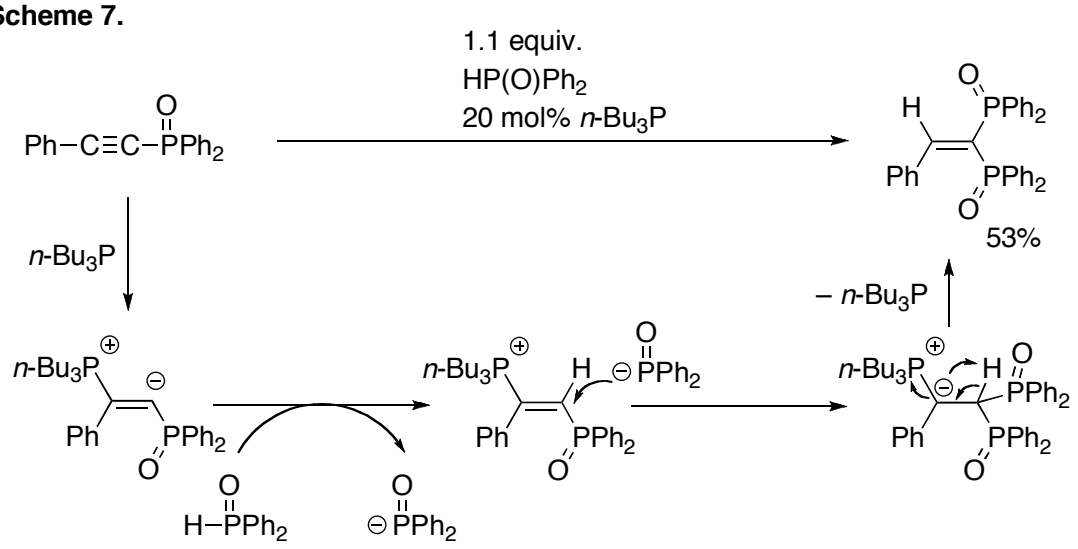
Addition reactions of nucleophiles to 1-alkynylphosphine derivatives are straightforward methods for the synthesis of 1-alkenylphosphine derivatives. The addition mainly occurs at the 2-position of the substrates. In the case of the addition of heteroatom nucleophiles such as hydrophosphines, thiols, and amines, the products are 1-alkenylphosphine derivatives containing a heteroatom substituent at the 2-position.

Hydrophosphination and Hydrophosphinylation

Ethynyldiphenylphosphine and bis(diphenylphosphino)ethyne undergo *syn*-hydrophosphination in the presence of strong bases such as phenyllithium and potassium *tert*-butoxide.[16] Upon complexation with stoichiometric amounts of platinum, palladium, or nickel, 1-alkynylphosphines participate in *anti*-hydrophosphination.[17]

Taran and co-workers reported α-addition of diphenylphosphine oxide to 1-alkynylphosphine oxides catalyzed by tributylphosphine (Scheme 7).[18] This reaction can provide a new route to P–C–P backbones.

Scheme 7.



Hydrothiolation

Under basic conditions, addition of thiols to 1-alkynylphosphine oxides and sulfides proceeds

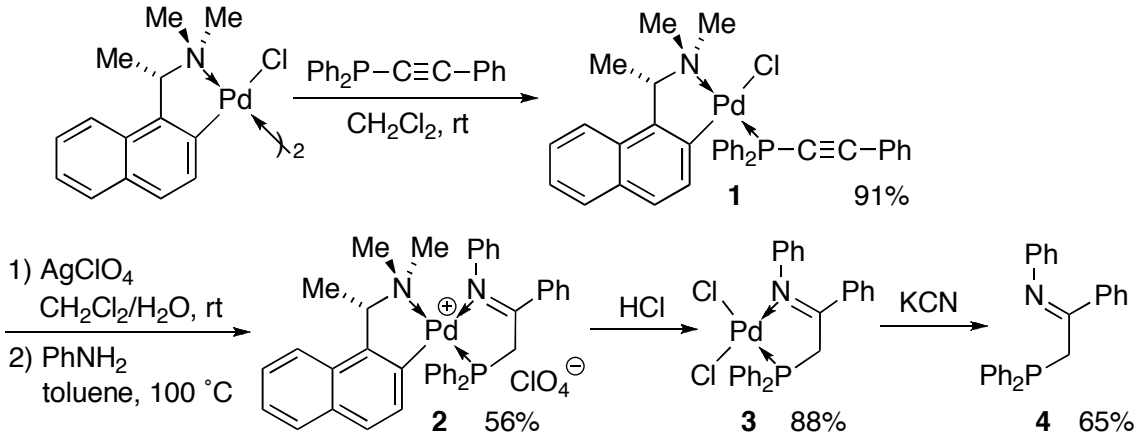
smoothly to afford 1-phosphinyl-2-thio-1-alkenes and 2-thio-1-thiophosphinyl-1-alkenes, respectively.[19] The addition proceeds regioselectively, while the stereoselectivity is low.

Hydroamination

In the presence or absence of strong bases such as butyllithium, nucleophilic addition of primary or secondary amines to 1-alkynyldiphenylphosphine oxides proceeds to provide 2-amino-1-phosphinyl-1-alkenes as a mixture of *E*/*Z* isomers.[20] Exceptionally, the addition to ethynyldiphenylphosphine oxide affords the *E* isomer exclusively.

Leung and co-workers reported hydroamination of 1-alkynylphosphines with aniline in the presence of an organopalladium template to give bidentate iminophosphines (Scheme 8).[21] The reaction started with regiospecific coordination of 1-alkynylphosphine onto the palladium complex to form the monomeric chloro complex **1**. After removal of the chloro ligand in **1** by means of silver perchlorate, the hydroamination of the resulting cationic palladium complex with aniline proceeded to form the iminophosphine complex **2**. The naphthylamine ligand on the template complex **2** could be removed chemoselectively by treatment with concentrated HCl to furnish dichloro complex **3**. The liberation of the iminophosphine ligand **4** from **3** was achieved by treatment of **3** with potassium cyanide. Iminophosphines are important ligands as potential catalyst supporters.[22]

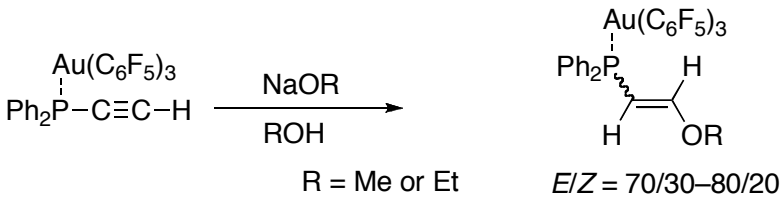
Scheme 8.



Addition of Other Nucleophiles

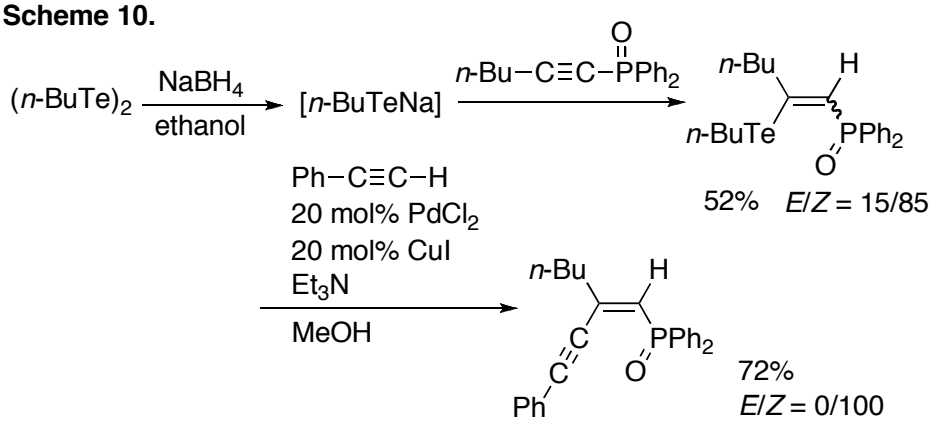
Michael addition of alcohols to 1-alkynylphosphine oxides is described in the literature.[23] In addition, *anti*-Markovnikov addition of methanol and ethanol to ethynylphosphine–gold complex was observed under basic conditions (Scheme 9).[24,25]

Scheme 9.



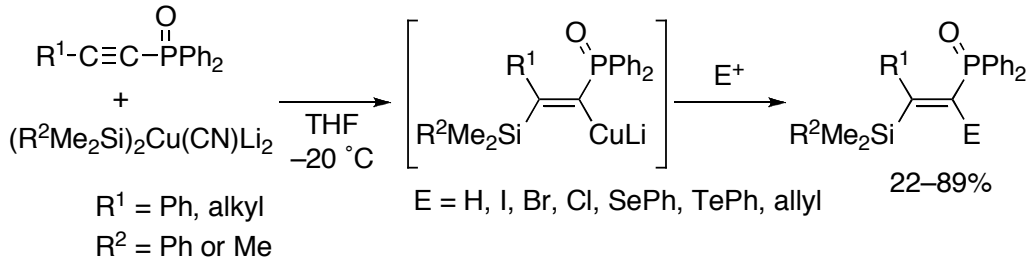
Hydrotelluration of 1-alkynylphosphine oxides afforded 2-telluro-1-alkenylphosphine oxides.[26] The adducts were subjected to cross-coupling with terminal alkynes under palladium catalysis to yield (*Z*)-2-alkynyl-1-alkenylphosphine oxides (Scheme 10).

Scheme 10.



Michael addition of silylcopper reagents to 1-alkynylphosphine oxides was reported by Huang and Xu.[27] This reaction proceeded in a *syn* fashion, and the resulting (*Z*)-alkenyl copper intermediate could be trapped with a variety of electrophiles to afford 2-silyl-substituted alkenylphosphine oxides (Scheme 11).

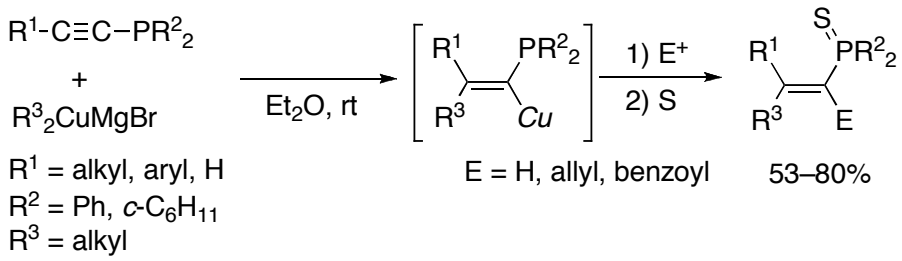
Scheme 11.



1.2.2. Carbometalation

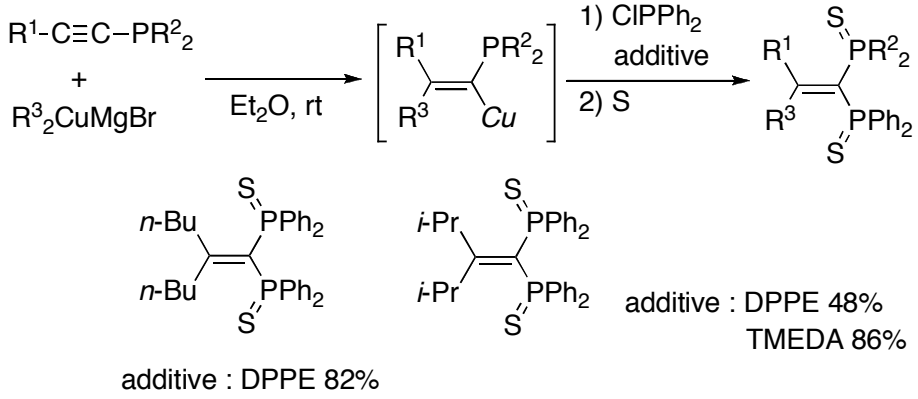
Carbometalation of 1-alkynylphosphine derivatives is an efficient method for the synthesis of polysubstituted alkenylphosphine derivatives. In 1976, Meijer and co-workers reported the addition of alkylcopper reagents to ethynyldiphenylphosphine and diphenyl(1-propynyl)phosphine.[28] Recently, Oshima, Yorimitsu and co-workers reported their detailed examination of carbocupration of 1-alkynylphosphines.[29] Addition of magnesium dialkylcuprate to 1-alkynylphosphines proceeded in a *syn* fashion to form alkenylcopper intermediate. Trapping of the intermediate with electrophiles such as allyl bromide and benzoyl chloride afforded tetrasubstituted alkenes in good yields (Scheme 12).

Scheme 12



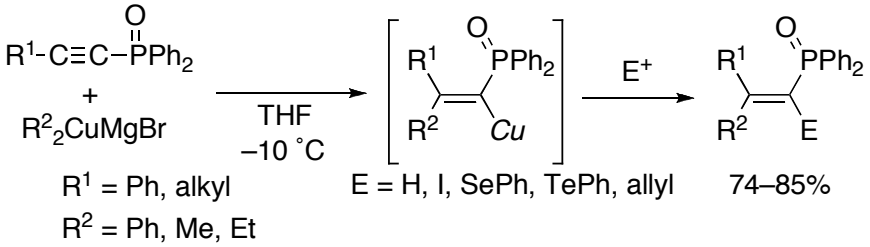
This reaction was applicable to the synthesis of *gem*-diphosphinoalkene derivatives, which were difficult to synthesize despite the interesting structure,[18,30] by trapping the intermediate with chlorodiphenylphosphine (Scheme 13). Interestingly, TMEDA or 1,2-bis(diphenylphosphino)-ethane proved to be essential as an additive for the trapping. Without the additive, only trace amounts of *gem*-diphosphinoalkenes were formed, and the protonated products were mainly obtained after aqueous work up.

Scheme 13



1-Alkynylphosphine oxides and 1-alkynylphosphine sulfides also undergo carbocupration.[31] Huang and Wu reported *syn*-carbocupration of 1-alkynylphosphine oxides.[31a] Not only dialkylcuprate but also diphenylcuprate reacted with 1-alkynylphosphine oxides to form alkenylcopper intermediate. The trapping of the intermediate with electrophiles afforded a variety of alkenylphosphine oxides in good yields (Scheme 14).

Scheme 14



1.3. Cycloaddition Reactions of 1-Alkynylphosphines and Their Derivatives

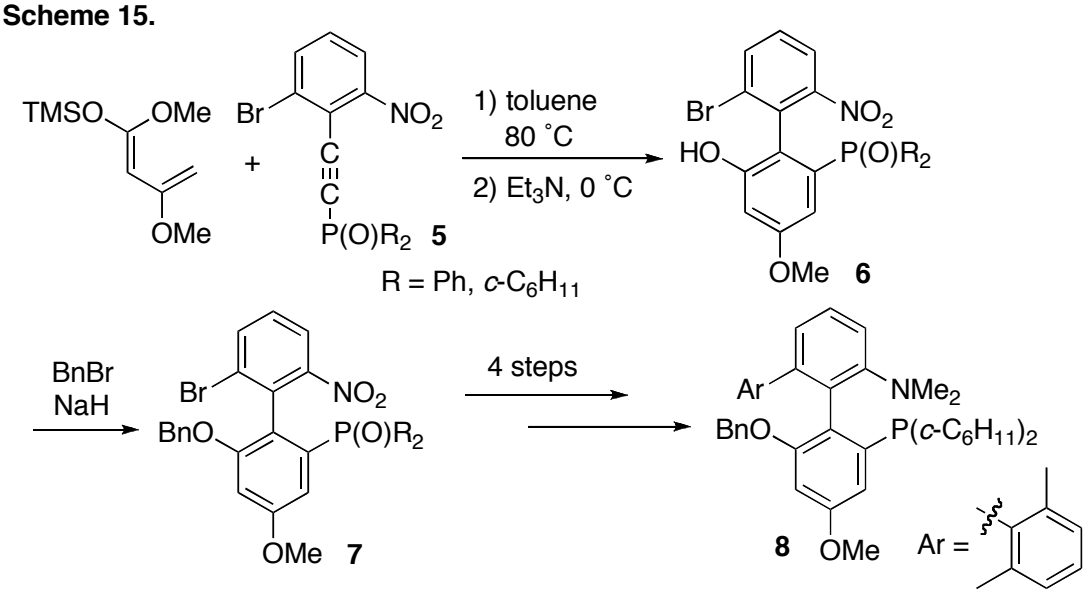
1.3.1. [4+2] Cycloaddition Reactions

Cycloaddition reactions of 1-alkynylphosphine derivatives lead to cyclic compounds containing a phosphorus substituent. This concept has been applied to the synthesis of new phosphines which are difficult to synthesize by other methods.

The Diels-Alder reaction is promising for this purpose. Carter and co-workers reported the synthesis of tri- and tetra-*ortho*-substituted phosphorus-containing biaryls using a Diels-Alder approach (Scheme 15).[32] Diels-Alder reaction of 1-alkynylphosphine oxide **5** with Brassard

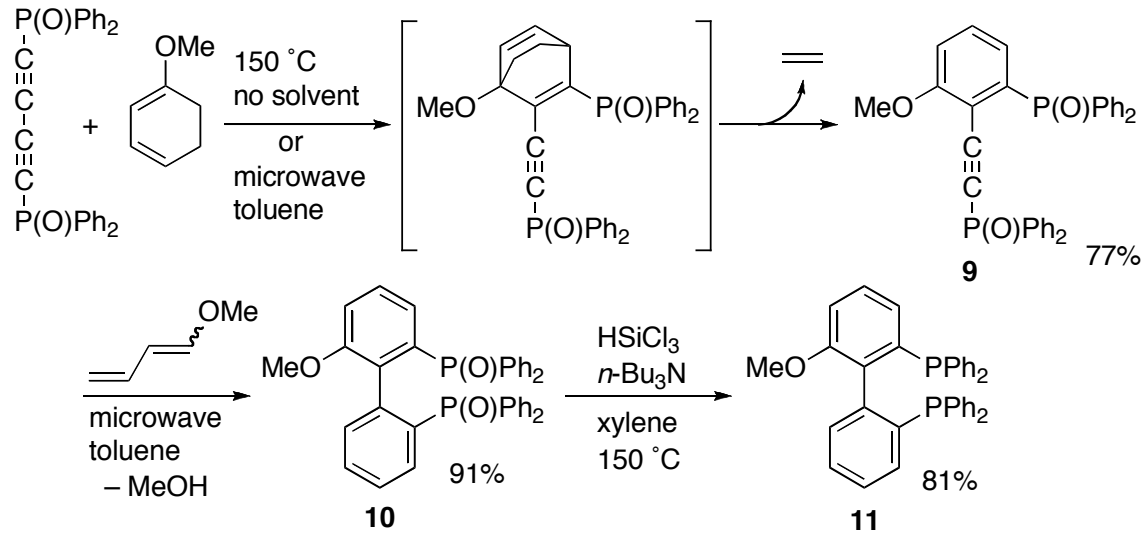
diene proceeded regioselectively. Aromatization followed by benzylation of the hydroxy group of **6** furnished biarylphosphine oxide **7**. Further transformation of **7** led to tetra-*ortho*-substituted biaryl **8**. The utility of the newly synthesized biarylphosphine **8** was shown in Suzuki-Miyaura cross-coupling reaction.

Scheme 15.



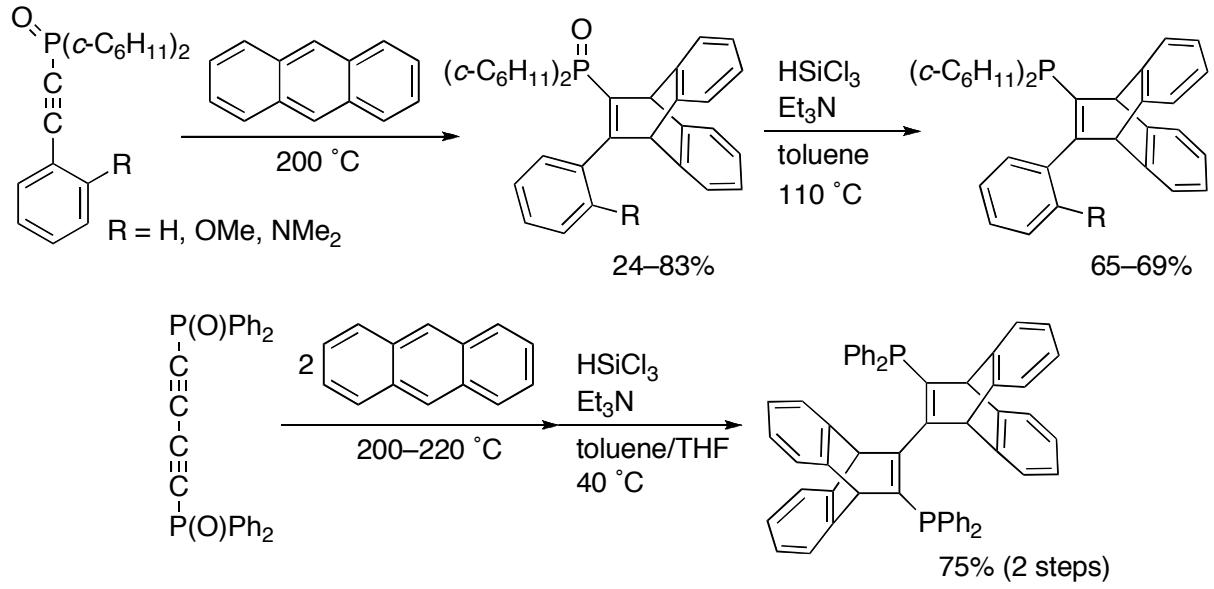
BIPHEP-type ligands are also accessible by the Diels-Alder approach. Doherty, Smyth and co-workers developed a stepwise regioselective double Diels-Alder cycloaddition-elimination sequence protocol (Scheme 16).[33] First, the reaction of 1,4-bis(diphenylphosphinyl)-1,3-butadiyne with 1-methoxy-1,3-cyclohexadiene proceeded regioselectively to form isolable monoadduct **9** with extrusion of ethylene. The second Diels-Alder reaction of **9** with 1-methoxy-1,3-butadiene followed by elimination of methanol furnished dissymmetric biaryl diphosphine dioxide **10**. Finally, the reduction of the phosphinyl groups of **10** by treating with trichlorosilane and tributylamine afforded biaryl diphosphine **11**. This stepwise cycloaddition-elimination sequence approach complements other approaches to dissymmetric atropos biaryl diphosphines.[34]

Scheme 16.



Doherty, Knight, Smyth and co-workers synthesized biaryl-like mono- and diphosphines via Diels-Alder reaction of 1-alkynylphosphine oxides with anthracene (Scheme 17).[35] These phosphines proved to serve as efficient ligands for palladium-catalyzed C–N and C–C bond formation reactions.

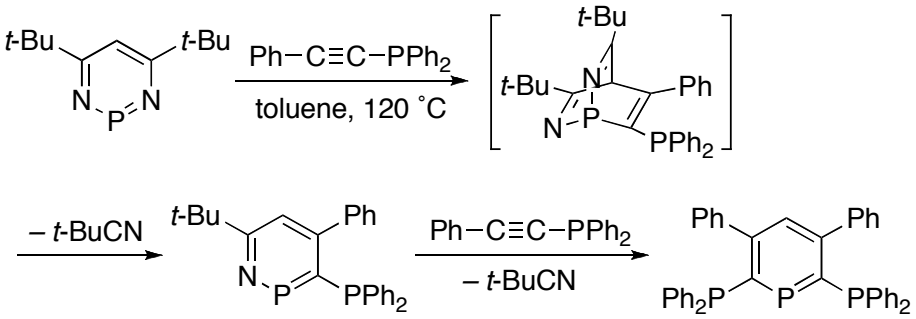
Scheme 17.



1,3,2-diazaphosphinines are versatile precursors of 1,2-azaphosphinines and polyfunctional

phosphinines.[36] They behave as diazaphosphacyclohexatrienes and participate in [4+2] cycloaddition with alkynes followed by cycloreversion to afford 1,2-azaphosphinines with extrusion of nitriles. 1,2-azaphosphinines can be converted to phosphinines by a similar process. The reaction of 1-alkynylphosphines with 1,3,2-diazaphosphinine afforded phosphinine which had two phosphino groups at the 2- and 6-positions (Scheme 18).[36a] 1-Alkynylphosphine oxides and sulfides also undergo similar [4+2] cycloaddition/elimination sequence with azaphosphinines to afford phosphinines having a phosphinyl or thiophosphinyl moiety.[37]

Scheme 18.

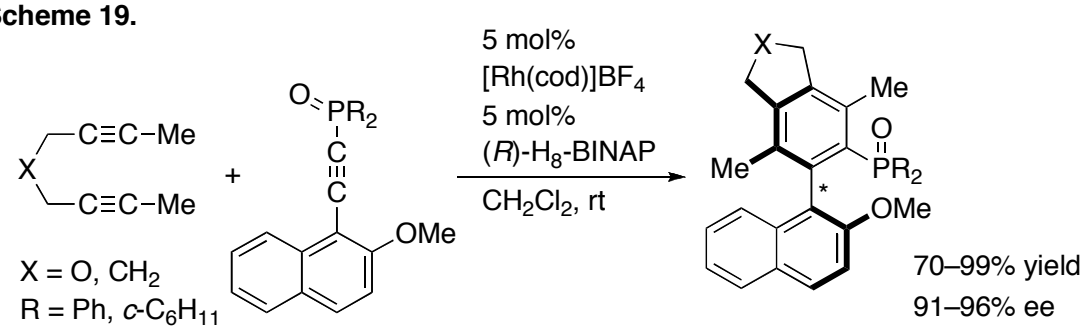


1.3.2. [2+2+2] Cycloaddition Reactions

Transition-metal-catalyzed [2+2+2] cycloaddition reactions of alkynes have received much attention due to their utility for the synthesis of substituted benzenes.[38] Recently, this methodology has been applied for the synthesis of new arylphosphines.

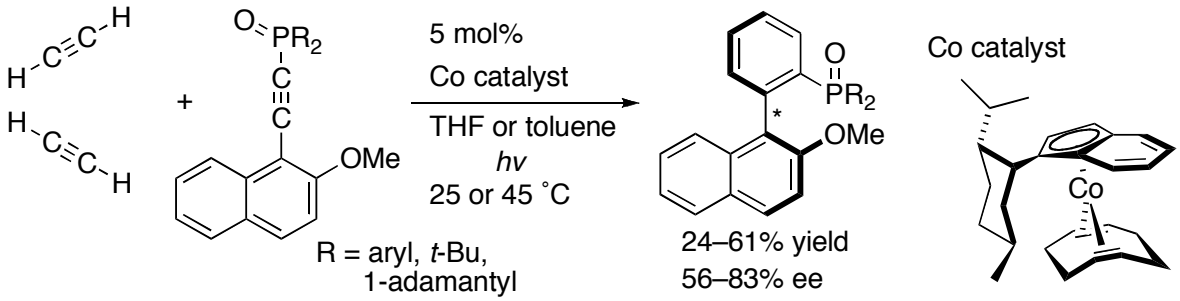
A practical method for the synthesis of axially chiral biaryl monophosphine oxides was developed by Tanaka and co-workers.[39] Enantioselective [2+2+2] cycloaddition of 2-naphthol-derived 1-alkynylphosphine oxides with 1,6-diynes in the presence of a cationic rhodium/H_8-BINAP catalyst furnished axially chiral phosphine oxides in high yield with high enantioselectivity (Scheme 19).

Scheme 19.



The synthesis of axially chiral biarylphosphine oxides was also accomplished under cobalt catalysis.[40,41] Heller and co-workers reported that enantioselective [2+2+2] cycloaddition of 1-alkynylphosphine oxides with acetylene proceeded in the presence of chiral cobalt catalyst to yield axially chiral biarylphosphine oxides (Scheme 20). Subsequent reduction of the product afforded the corresponding phosphines. The utility of the newly synthesized phosphine was demonstrated in palladium-catalyzed asymmetric hydrosilylation of alkenes.

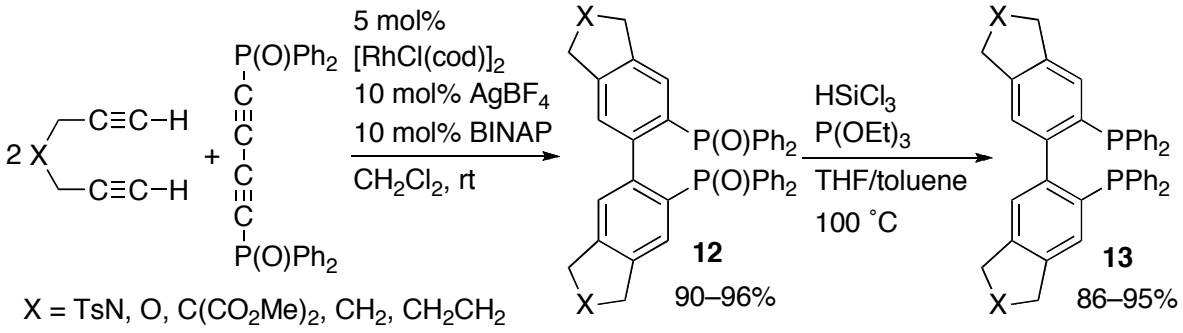
Scheme 20.



The application of the [2+2+2] cycloaddition approach to the synthesis of biaryl diphosphines was reported by Doherty and co-workers.[42,43] They reported that the double [2+2+2] cycloaddition of 1,4-bis(diphenylphosphinyl)-1,3-butadiyne with tethered diynes proceeded in the presence of a cationic rhodium/BINAP catalyst to furnish biaryl diphosphine dioxides in high yields (Scheme 21). Enantiopure platinum complexes of biaryl diphosphines **13**, which were obtained by the reduction of **12** followed by optical resolution using enantiopure BINOL as a resolving agent, were highly efficient catalysts for asymmetric carbonyl-ene reactions and Diels-Alder reactions. They also reported the highly enantioselective synthesis of axially chiral

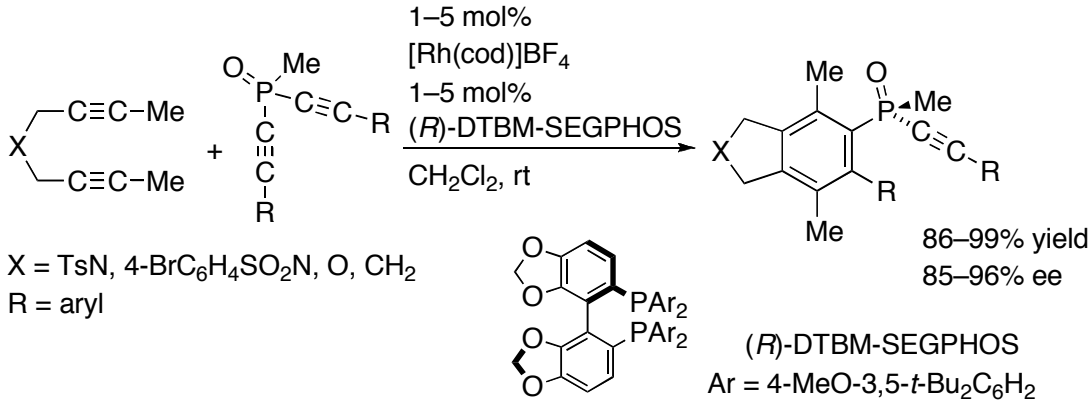
biaryl diphosphine dioxides via stepwise double [2+2+2] cycloadditions.[42b]

Scheme 21.



The other application of the [2+2+2] cycloaddition approach is the construction of P-stereogenic center. Tanaka and co-workers reported enantioselective synthesis of P-stereogenic 1-alkynylphosphine oxides by rhodium-catalyzed [2+2+2] cycloaddition of symmetrical dialkynylphosphine oxides with 1,6-diynes (Scheme 22).[44]

Scheme 22.



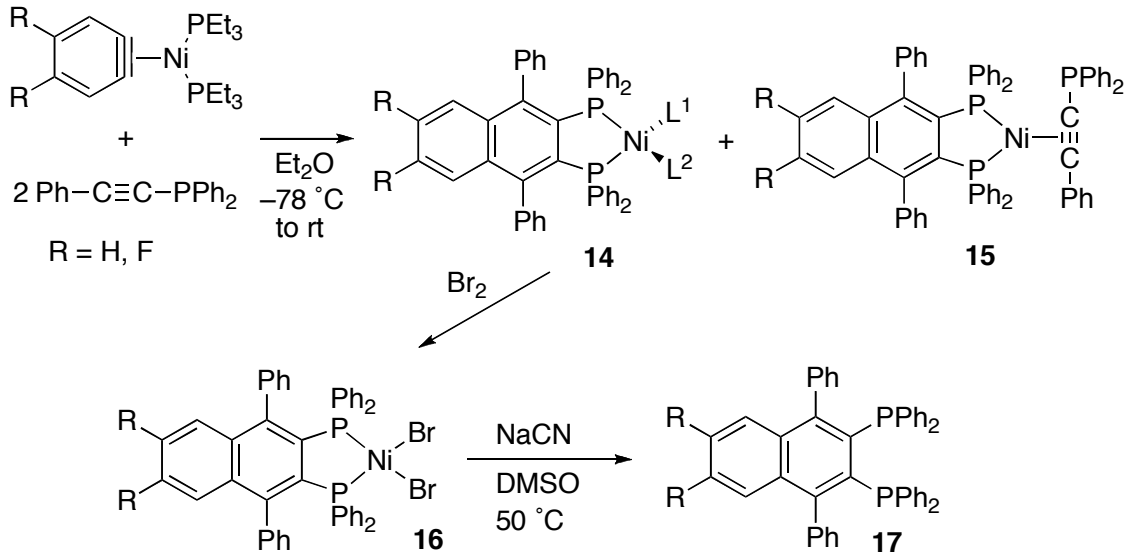
1.4. Miscellaneous Reactions

Nickel-Mediated Reactions

Bennett and co-workers reported the regiospecific synthesis of 2,3-bis(diphosphino)naphthalenes by double insertion of 1-alkynylphosphines into nickel(0)–benzyne complexes.[45] Nickel(0)–benzyne complex reacted with two equivalents of 1-alkynyldiphenylphosphines to form a mixture of nickel complexes **14** and **15**. Treatment of the mixture with bromine afforded dibromonickel complex **16**. Reaction of **16** with sodium

cyanide in dimethyl sulfoxide liberated pure 2,3-bis(diphenylphosphino)naphthalene **17** (Scheme 23).

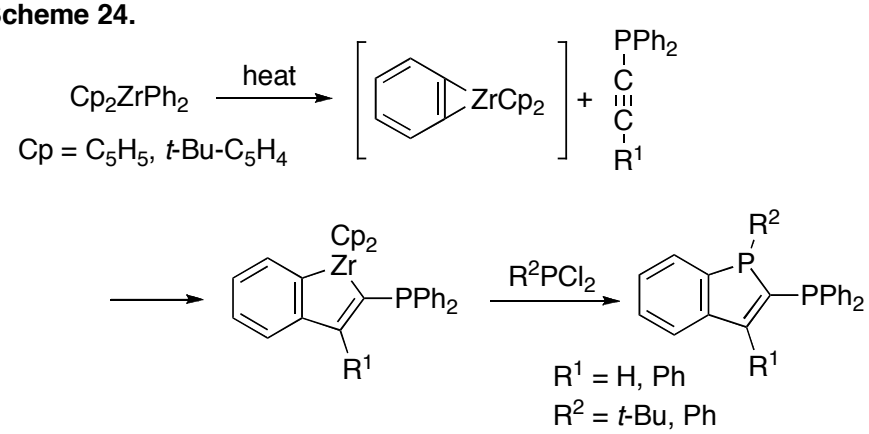
Scheme 23.



Zirconium-Mediated Reactions

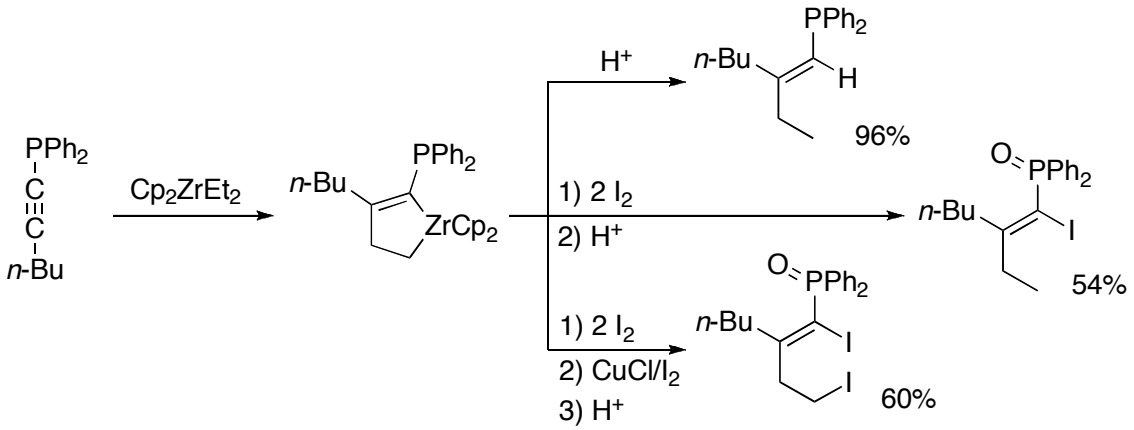
Zirconocene–benzyne complexes also react with 1-alkynylphosphines.[46,47] Majoral and co-workers reported that treatment of 1-alkynylphosphine with zirconocene complex led to the formation of phosphinozirconaindene arising from regioselective insertion of carbon–carbon triple bond of 1-alkynylphosphine into a zirconium–carbon bond of the transient zirconocene–benzyne complex. The reactions of phosphinozirconaindenes with dichlorophosphines afforded 2-phosphinophosphole derivatives (Scheme 24).

Scheme 24.

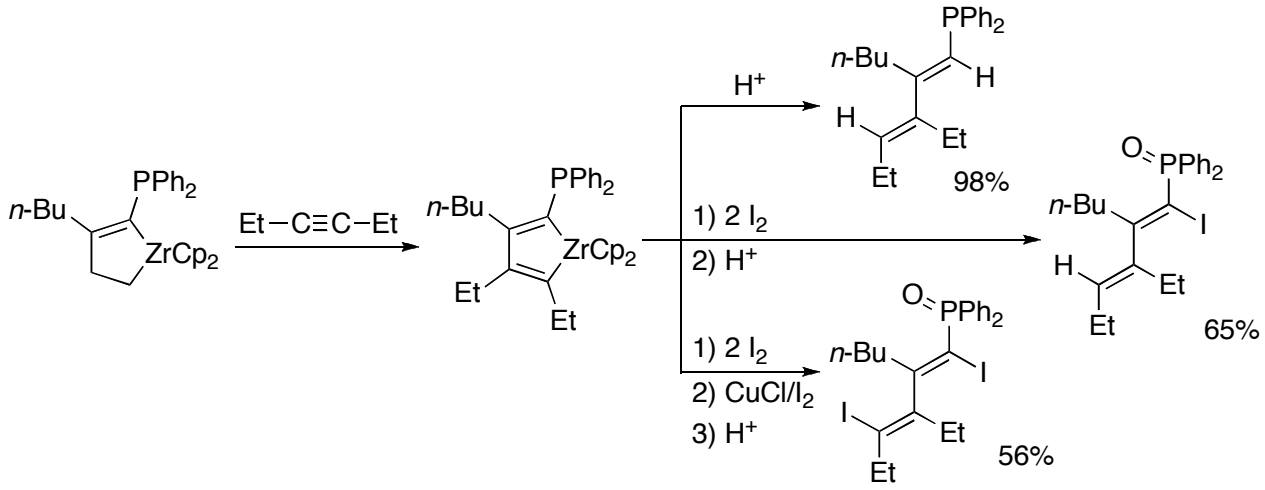


Xi, Takahashi and Zhang developed zirconocene-mediated reactions of 1-alkynylphosphines with ethylene or simple alkynes.[48] Treatment of 1-alkynylphosphines with zirconocene ethylene complex generated in situ led to the formation of α-phosphinozirconacyclopentenes. Protonation or iodination of this intermediate furnished 1-alkenylphosphine derivatives in good yields (Scheme 25). The reactions of α-phosphinozirconacyclopentenes with alkynes afforded α-phosphinozirconacyclopentadienes.[49] Protonation or iodination furnished 1,3-alkadienylphosphine derivatives (Scheme 26).

Scheme 25.



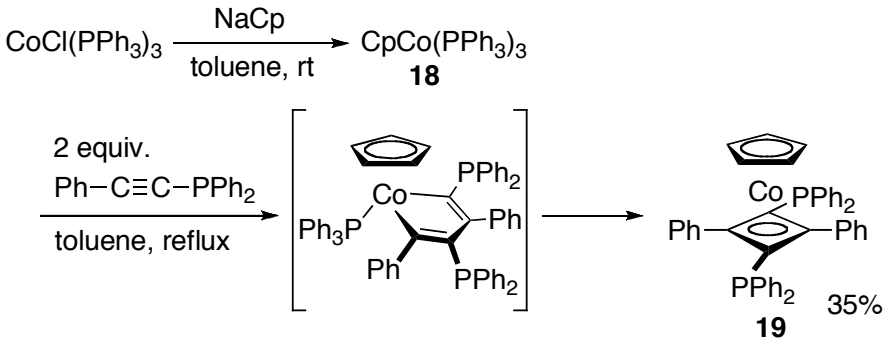
Scheme 26.



Cobalt-Mediated Reactions

Hong and co-workers investigated the reaction of cobalt complex **18** with 1-alkynylphosphines.[50] The reaction provided cobalt-containing diphosphine **19**, which was employed as a ligand in Suzuki-Miyaura cross-coupling reaction (Scheme 27).

Scheme 27.



2. Overview of This Thesis

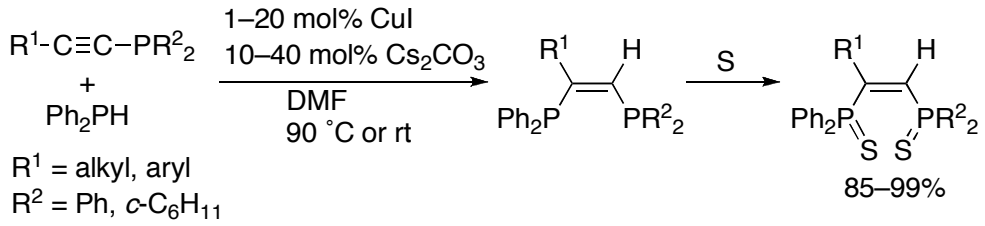
The author focused on 1-alkynylphosphines and 1-alkynylphosphine sulfides as precursors of new phosphines, and developed several methods for the synthesis of various phosphines starting from 1-alkynylphosphines and 1-alkynylphosphine sulfides. In Chapters 1–3, addition reactions of heteroatom nucleophiles such as diphenylphosphine, thiols, and amides to 1-alkynylphosphine derivatives are disclosed. In Chapters 4 and 5, conceptually novel approaches to bulky

arylphosphines and heteroarylphosphines are described. In Chapter 6, an intriguing transformation of 1-alkynylphosphines to (*E*)-1-alkenyphosphine oxides is disclosed. The methods described in this thesis not only provide a variety of new phosphines that are otherwise difficult to synthesize but also offer creative and reliable approaches to phosphines. Considering the importance of phosphines in organic synthesis, especially as ligands, this study would contribute to the advancement in various fields of chemistry.

2.1. Copper-Catalyzed *anti*-Hydrophosphination Reaction of 1-Alkynylphosphines with Diphenylphosphine Providing (*Z*)-1,2-Diphosphino-1-alkenes (Chapter 1)

Hydrophosphination of unsaturated substrates, that is addition of trivalent hydrophosphines across multiple bonds, represents a straightforward method for the synthesis of organophosphines.[51] In Chapter 1, the author describes copper-catalyzed *anti*-hydrophosphination reaction of 1-alkynylphosphines with diphenylphosphine. Treatment of 1-alkynylphosphines with diphenylphosphine in the presence of catalytic amounts of copper iodide and cesium carbonate in DMF afforded (*Z*)-1,2-diphosphino-1-alkenes in good yields with perfect regio- and stereoselectivity (Scheme 28). The diphosphines obtained are not only structurally intriguing entities but also potentially useful ligands for transition metals. Despite their potential, the efficient synthesis of (*Z*)-1,2-diphosphino-1-alkenes has been scarcely reported so far.[16,17]

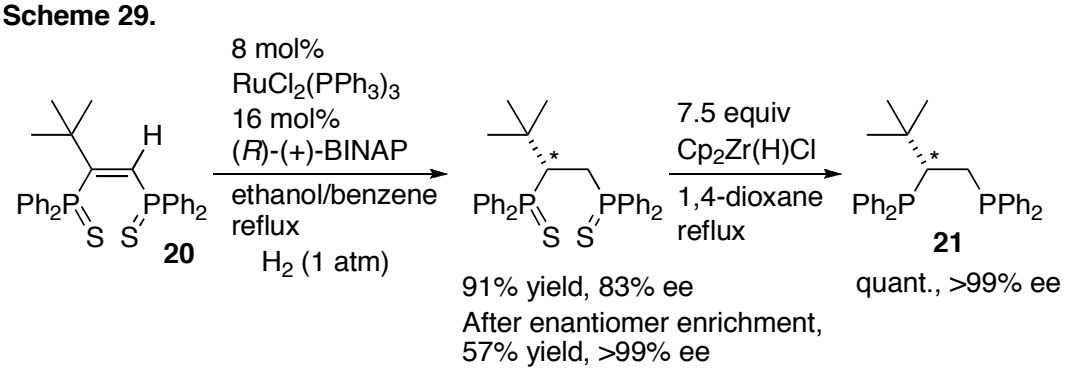
Scheme 28.



The reaction is highly chemoselective and can be performed even in an aqueous medium. The adducts, diphosphine disulfides, could be easily reduced to the parent trivalent diphosphines

under radical desulfidation conditions. Enantioselective hydrogenation of diphosphine disulfide **20** followed by desulfidation afforded new chiral bidentate phosphine **21** (Scheme 29). The sequential phosphination/hydrogenation protocol offers an alternative to the conventional approach to chiral bidentate diphosphines.

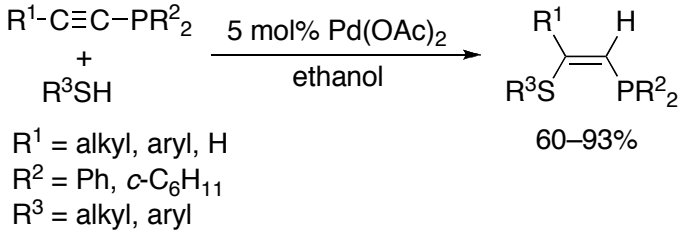
Scheme 29.



2.2. Palladium-Catalyzed *anti*-Hydrothiolation of 1-Alkynylphosphines

Addition of thiols to alkynes (hydrothiolation) is an important reaction for synthesizing 1-alkenylsulfides. In Chapter 2, the author shows palladium-catalyzed *anti*-hydrothiolation of 1-alkynylphosphines. Treatment of 1-alkynylphosphines with thiols in the presence of a catalytic amount of palladium acetate in ethanol resulted in regio- and stereoselective *anti*-hydrothiolation (Scheme 30). In general, transition-metal-catalyzed hydrothiolation proceeds in a *syn* fashion.[51b,52] In contrast, the present reaction represents a rare example of highly selective *anti*-hydrothiolation.[53] The products, (*Z*)-1-phosphino-2-thio-1-alkenes, are a new class of heteroatom-containing compounds and can potentially serve as useful ligands of transition-metal complexes.

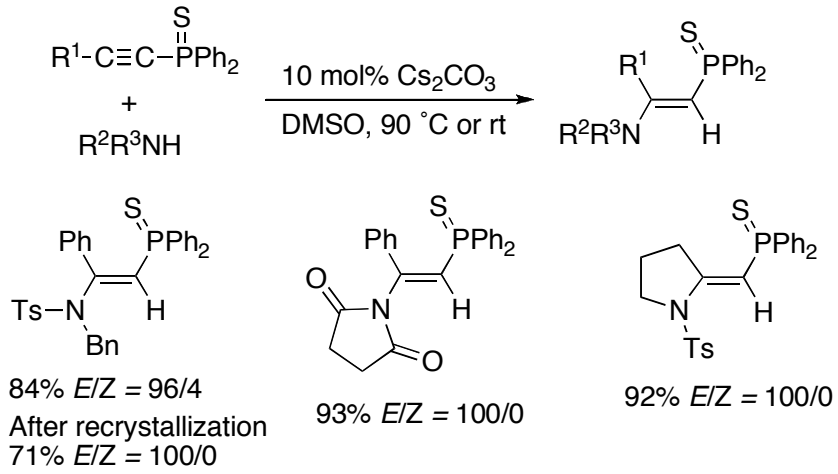
Scheme 30.



2.3. Regio- and Stereoselective Hydroamidation of 1-Alkynylphosphine Sulfides Catalyzed by Cesium Base

In Chapter 3, the author shows cesium-catalyzed addition of amides or imides to 1-alkynylphosphine sulfides, directed toward the construction of vicinal N,P-frameworks (Scheme 31).

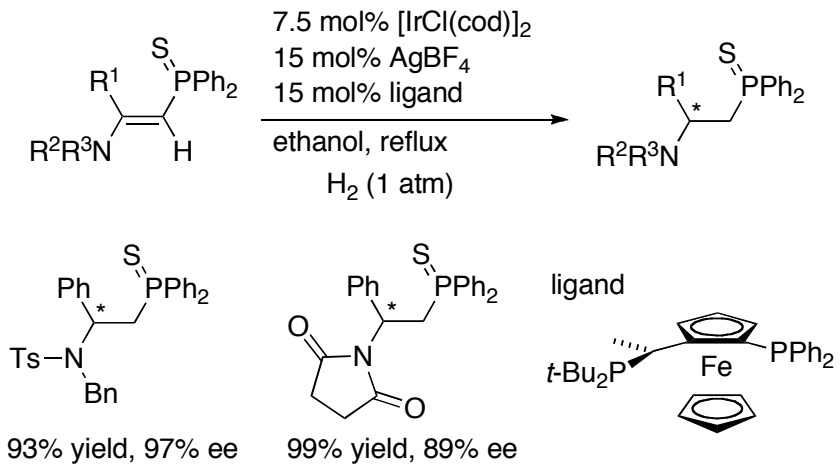
Scheme 31.



This addition proceeded mainly in a *syn* fashion, and recrystallization of the products allowed for the isolation of the major *E* isomers. The amidation was applicable to intramolecular cyclizations.

The adducts underwent enantioselective hydrogenation catalyzed by a cationic iridium complex (Scheme 32). The sequential hydroamidation/hydrogenation protocol offers a new approach to chiral N,P-ligands that will potentially serve as ligands in asymmetric reactions. The phosphine sulfides synthesized by hydroamidation/hydrogenation could be easily reduced to the corresponding trivalent phosphines under radical desulfidation conditions.

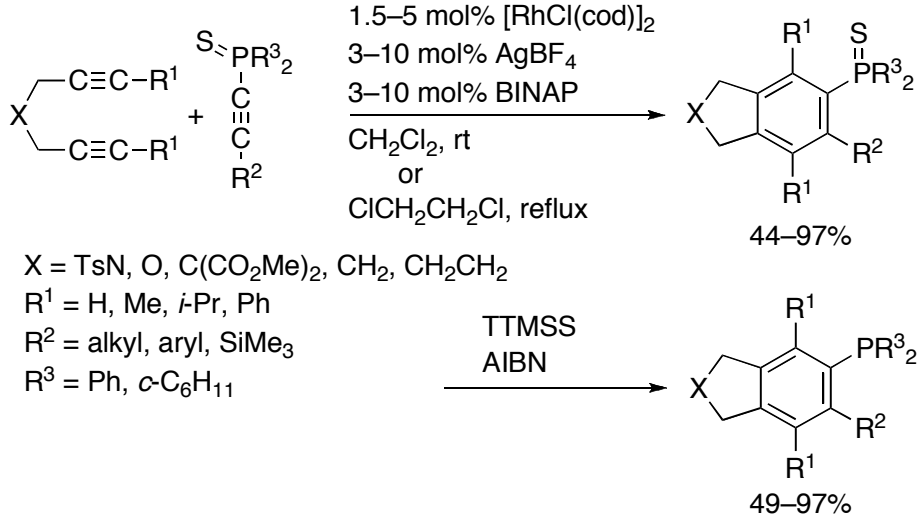
Scheme 32.



2.4. Synthesis of Bulky Phosphines by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides

In the past decade, bulky triorganophosphines have attracted increasing attention as excellent ligands for transition metal catalysts in preparing biologically intriguing compounds as well as functional organic materials.[1c,54] Synthesis of such ligands is hence quite important. In Chapter 4, the author describes rhodium-catalyzed formal [2+2+2] cycloaddition reactions of 1-alkynylphosphine sulfides with tethered diynes, which offer a conceptually new approach to bulky phosphines. Treatment of a variety of 1-alkynylphosphine sulfides with tethered diynes in the presence of a cationic rhodium catalyst and BINAP afforded arylphosphine sulfides in good yields (Scheme 33).

Scheme 33.



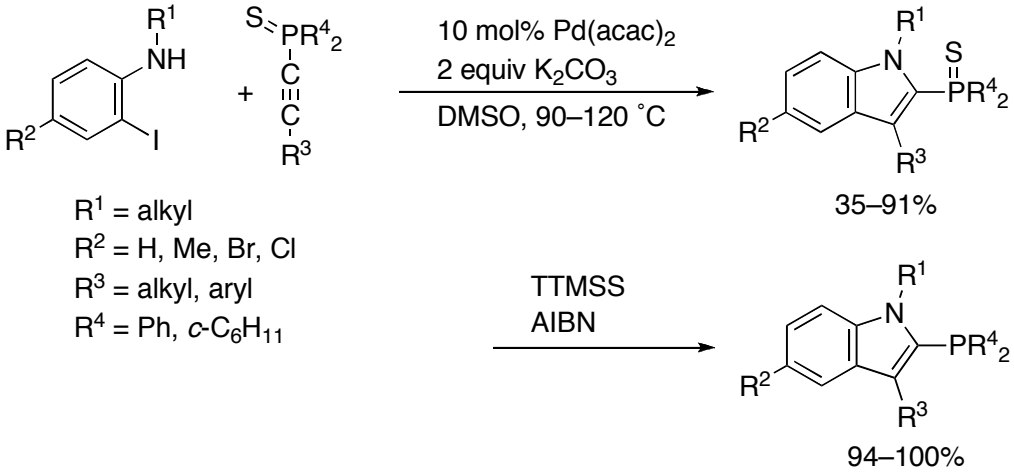
The newly formed benzene rings have one or two substituents next to the thiophosphinyl group, which provide sterically congested environment around the phosphorus. The product, phosphine sulfides, could be easily converted to the corresponding bulky phosphines under radical desulfidation conditions. Dicyclohexyl(2,6-diphenylaryl)phosphine, which was synthesized by this method, proved to serve as an efficient ligand in palladium-catalyzed amination of aryl chloride with morpholine.

2.5. New Synthesis of 2-Indolylphosphines by Palladium-Catalyzed Annulation of 1-Alkynylphosphine Sulfides with 2-Iodoanilines

In Chapter 5, the author focuses on the conceptually new approach to 2-indolylphosphines by using 1-alkynylphosphine sulfides as starting materials. Treatment of 1-alkynylphosphine sulfides with *N*-alkyl-2-iodoanilines in the presence of (acetylacetonato)palladium and potassium carbonate afforded 2-indolylphosphine sulfides in good yields (Scheme 34).

The newly formed indole rings naturally have a substituent derived from 1-alkynylphosphine sulfides next to the thiophosphinyl group, which creates sterically hindered environment around the phosphorus. The products could be easily reduced to the corresponding trivalent phosphines under radical desulfidation conditions.

Scheme 34.

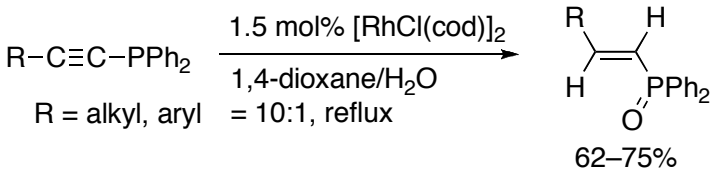


R^1 = alkyl
R^2 = H, Me, Br, Cl
R^3 = alkyl, aryl
R^4 = Ph, *c*-C_6H_{11}

2.6. Rhodium-Catalyzed Reaction of 1-Alkynylphosphines with Water Yielding (*E*)-1-Alkenylphosphine Oxides

In Chapter 6, a formal hydration reaction of 1-alkynylphosphines is described. Treatment of 1-alkynylphosphines with a rhodium catalyst in 1,4-dioxane/H_2O provided (*E*)-1-alkenylphosphine oxides (Scheme 35).

Scheme 35.



The reaction proceeds as follows. First, oxidative addition of 1-alkynylphosphine to rhodium followed by hydrolysis yields the corresponding terminal alkyne and diphenylphosphine oxide. Next, rhodium-catalyzed hydrophosphinylation of the terminal alkyne, which is generated in the first step, with diphenylphosphine oxide proceeds to afford (*E*)-1-alkenylphosphine oxide.

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Chapter 1

Copper-Catalyzed *anti*-Hydrophosphination Reaction of 1-Alkynylphosphines with Diphenylphosphine Providing (*Z*)-1,2-Diphosphino-1-alkenes

Hydrophosphination of 1-alkynylphosphines with diphenylphosphine proceeds in an *anti* fashion under copper catalysis, providing an easy and efficient access to a variety of (*Z*)-1,2-diphosphino-1-alkenes and their sulfides. Radical reduction of the diphosphine disulfides with tris(trimethylsilyl)silane yields the parent trivalent diphosphines without suffering from the isomerization of the olefinic geometry. Enantioselective hydrogenation of (*Z*)-3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene followed by desulfidation leads to a new chiral bidentate phosphine ligand.

Introduction

Organophosphines have been gaining in importance as ligands for transition metal catalysts, as clearly demonstrated in cross-coupling reactions[1] and asymmetric transformations.[2] Creation of new organophosphines and, naturally, of new phosphination reactions can thus have great impact on various fields of chemical science.

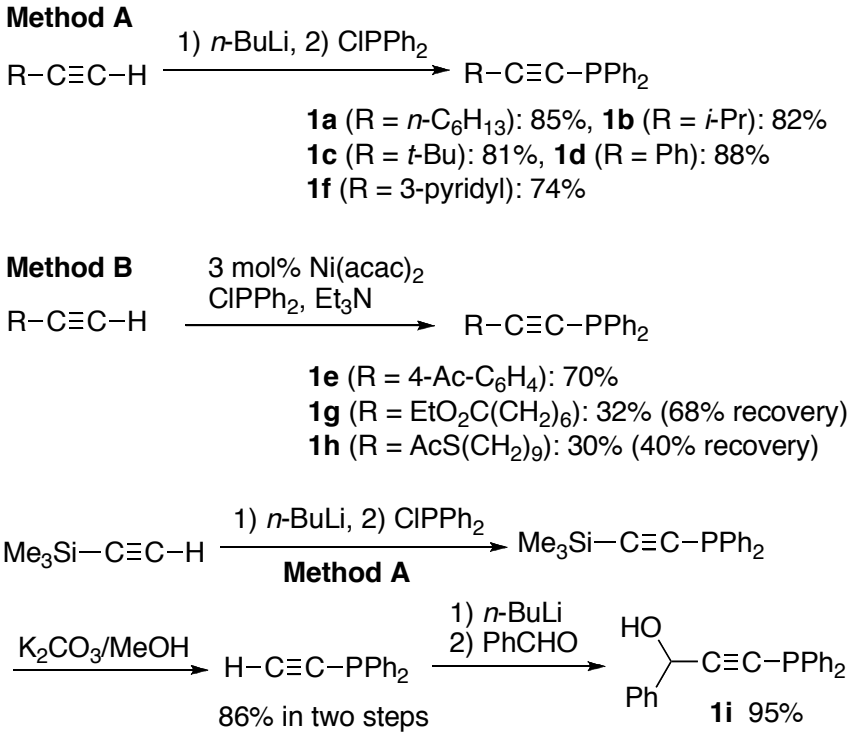
Metal-catalyzed hydrophosphination reactions of C–C multiple bonds represent a straightforward method for the synthesis of organophosphines.[3] In particular, catalytic hydrophosphinations of phosphorus-substituted unsaturated C–C bonds seem to be quite useful since the reactions provide bidentate diphosphines. In spite of their potential utility, the hydrophosphinations providing bidentate phosphines are rather limited. Although the hydrophosphinations of vinylphosphines proceed smoothly in the presence of a base to afford useful 1,2-diphosphinoethanes, the hydrophosphinations require the native vinyl group, i.e., $(CH_2=CH)_nPR_{3-n}$.[4,5]

In this chapter, the author focuses on 1-alkynylphosphines as the substrates. The precedent hydrophosphinations of 1-alkynylphosphines highlight the difficulty in achieving the transformation. Ethynyldiphenylphosphine and bis(diphenylphopshino)ethyne undergo *syn*-hydrophosphination in the presence of strong bases such as phenyllithium.[4b,6] Upon complexation with platinum, palladium or nickel, 1-alkynylphosphines of some generality participate in *anti*-hydrophosphination.[7] The use of stoichiometric amounts of expensive transition metals is a definite and significant drawback. Here the author describes that hydrophosphinations of various 1-alkynylphosphines with diphenylphosphine proceed in an *anti* fashion under copper catalysis with perfect stereo- and regioselectivity. The diphosphines obtained, (*Z*)-1,2-diphosphino-1-alkenes, are not only structurally intriguing entities but also potentially useful bidentate ligands for transition metals. Furthermore, the carbon–carbon double bonds of the diphosphines can enjoy further functionalizations. Despite their latent rich chemistry, efficient and general methods for the synthesis of (*Z*)-1,2-diphosphino-1-alkenes have scarcely been reported so far.[8,9]

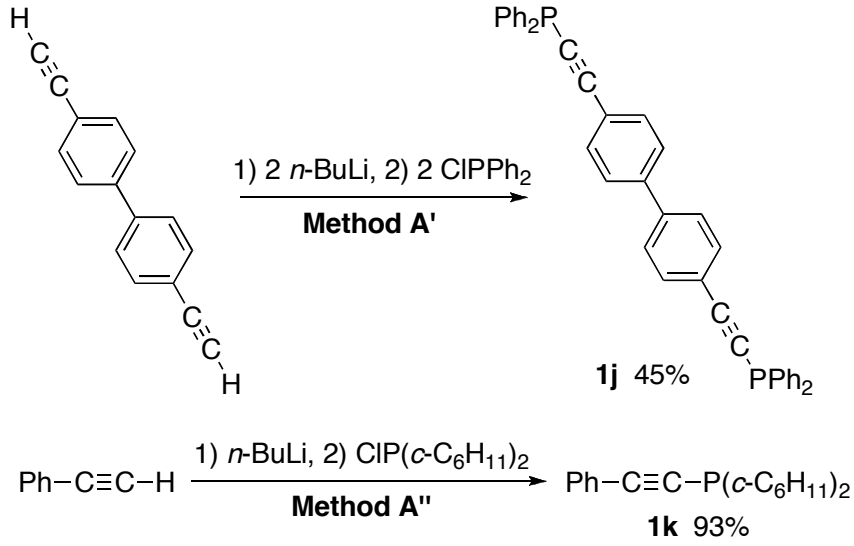
Results and Discussion

Preparation of 1-Alkynylphosphines. Starting alkynes **1** were prepared by nucleophilic substitution reactions of chlorophosphines with 1-lithio-1-alkynes (Scheme 1, method A) or nickel-catalyzed coupling reactions of chlorodiphenylphosphine and terminal alkynes in the presence of triethylamine (method B).[10] Whereas method A was high-yielding, method B was suitable for the synthesis of **1** having labile functional groups. The nickel-catalyzed reactions of aliphatic alkynes did not go to completion (**1g**, **1h**). Alkynylphosphine **1i**, having a hydroxy group, was available in three steps, i.e., preparation of diphenyl(trimethylsilylethynyl)phosphine by method A, protodesilylation, and nucleophilic addition of diphenylphosphinoethynyllithium to benzaldehyde. Diphosphine **1j** was prepared by the dilithiation of 4,4'-diethynylbiphenyl followed by the reaction with chlorodiphenylphosphine (method A'). Aliphatic phosphine **1k** was prepared in fashions similar to method A by using chlorodicyclohexylphosphine (method A'').

Scheme 1.



Scheme 1. (Continued)



Hydrophosphination Reactions of 1-Alkynylphosphines. Treatment of 1-octynyldiphenylphosphine (**1a**) with diphenylphosphine in the presence of catalytic amounts of copper(I) iodide and cesium carbonate in *N*,*N*-dimethylformamide (DMF) at 25 ˚C yielded (*Z*)-1,2-bis(diphenylphosphino)-1-octene (**2a**) exclusively (Table 1, entry 1). Handling of **2a** under air for purification led to gradual oxidation. To evaluate the efficiency of the reaction accurately, the author isolated the product as phosphine sulfide **3a** after treatment with crystalline sulfur. Isolation of the parent phosphine **2a** and its analogues is discussed in the following section. The yield of **3a** based on ^{31}P NMR was 99%, and the isolated yield was 88%. The formation of the *Z* isomer was determined by the coupling constant of $J(^{31}P–^{31}P)$ of **3a** (16 Hz), whereas (*E*)-1,2-bis(diphenylthiophosphinyl)-1-alkenes and 1,1-bis(diphenylthiophosphinyl)-1-alkenes exhibit ca. 50 and 30 Hz of $J(^{31}P–^{31}P)$, respectively.[11]

Aprotic polar solvents are the choice of solvents. The reactions in dimethyl sulfoxide, THF, and ether afforded **3a** in 94%, 62%, and 0% NMR yields, respectively, under the otherwise same reaction conditions. Surprisingly, the reaction in aqueous DMF (1:1) also provided **3a** in 82% yield.

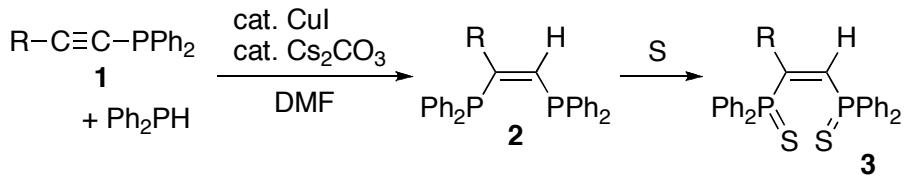
Copper(I) iodide is the best among transition metal catalysts the author tested. Copper(I)

chloride was as effective as CuI (98% yield). Other copper salts such as CuCN, CuBr, $CuBr{\cdot}Me_2S$, and $CuCl_2$ also effected the hydrophosphination albeit the yields were lower (10%, 57%, 87%, and 84%, respectively). Neither metallic copper, CuO, nor Cu_2O are inactive. Silver(I) iodide (5 mol% in DMSO) also served to afford **3a** in 88% yield. None of gold(I) chloride, nickel(II) chloride, or cobalt(II) chloride exhibited any catalytic activity. The use of 5 mol% of palladium(II) chloride or platinum(II) chloride yielded **3a** in 5% yield, which invokes the formation of a stable and catalytically inactive palladium or platinum complex in the reaction mixture.[7] It is worth noting that a diphenylphosphide anion has been regarded as an untransferable dummy ligand in cuprate chemistry.[12]

The use of Cs_2CO_3 is crucial. Potassium carbonate, sodium carbonate, and triethylamine promoted the hydrophosphination reaction much less effectively (18%, 3%, and 2% yields, respectively). Neutral CsCl did not induce the reaction. Instead of the CuI/Cs_2CO_3/DMF system, a CuI (10 mol%)/*n*-BuLi (20 mol%)/THF system was effective yet led to slower conversion (4 h, 49%; 8 h, 76%; 20 h, 86%). Without copper salts, Cs_2CO_3 by itself could not promote the reaction. Although butyllithium alone could effect the hydrophosphination in THF at ambient temperature, the reaction afforded a mixture of the *Z* and *E* isomers in 27% and 70 % yields, respectively.

A wide range of 1-alkynylphosphines **1** were subjected to the phosphination reaction (Table 1). Sterically demanding 1-alkynylphosphines including **1b** and **1c** underwent the hydrophosphination smoothly, although higher catalyst loadings were required to complete the reaction (Table 1, entries 2 and 4). An elevated temperature also facilitated the reaction of **1c** (Table 1, entry 3). A variety of functional groups such as keto and hydroxy groups were compatible under the reaction conditions (Table 1, entries 6–10), whereas known hydrophosphination reactions of alkynes were generally unsatisfactory with regard to the functional group compatibility.[13] Pyridine-containing **2f** or **3f** (Table 1, entry 7) and sulfur-containing **2h** or **3h** (Table 1, entry 9) can be useful for constructing supramolecular architectures.

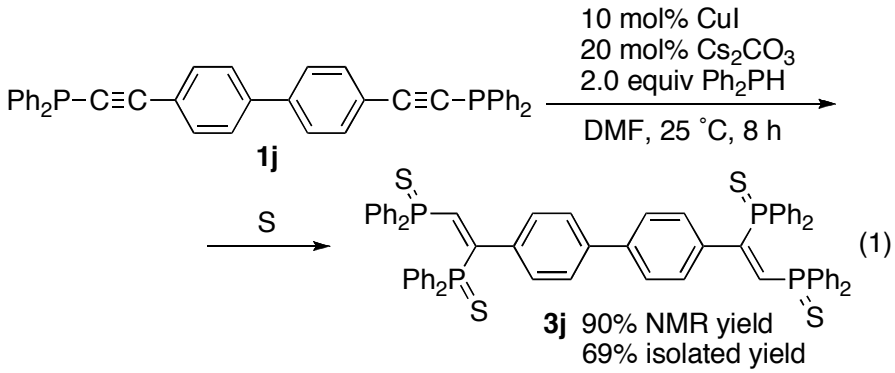
Table 1. Copper-Catalyzed Hydrophosphination of 1-Alkynylphosphines with Diphenylphosphine[a]

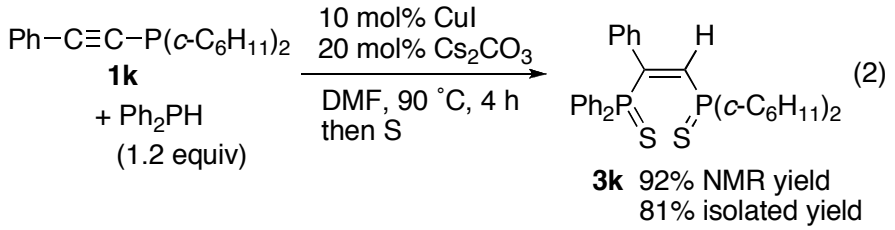


entry	R	CuI /mol%	Cs_2CO_3 /mol%	yield of **3** /%[b]
1	*n*-C_6H_{13} (**a**)	1	10	99 (88)
2[c]	*i*-Pr (**b**)	10	20	98 (84)
3[d]	*t*-Bu (**c**)	2	10	99 (87)
4[c]	*t*-Bu (**c**)	10	20	90 (84)
5	Ph (**d**)	1	10	98 (72)
6	4-Ac-C_6H_4 (**e**)	10	20	98 (87)
7	3-pyridyl (**f**)	2	10	88 (62)
8	$EtO_2C(CH_2)_6$ (**g**)	2	10	85 (79)
9[e]	$AcS(CH_2)_9$ (**h**)	20	40	94 (75)
10	PhCH(OH) (**i**)	10	20	87 (84)

[a] Hydrophosphination conditions: **1** (0.50 mmol), Ph_2PH (0.60 mmol), DMF (3.0 mL), 25 ˚C, 4 h. Sulfidation conditions: sulfur (2.0 mmol), 25 ˚C, 1 h. [b] Based on ^{31}P NMR with a sufficient first decay period. Isolated yields are in parentheses.
[c] The reaction was performed for 6 h. [d] The reaction was performed at 90 ˚C.
[e] The reaction was performed for 20 h.

The reaction was efficient enough to provide tetraphosphine sulfide **3j** in excellent yield (eq 1). Although hydrophosphination across **1k** having a dicyclohexylphosphino group at 25 ˚C led to complete recovery of **1k**, the anticipated **3k** could be prepared at 90 ˚C (eq 2). Attempts to perform the addition of dicyclohexylphosphine to **1a** or **1d** resulted in failure.

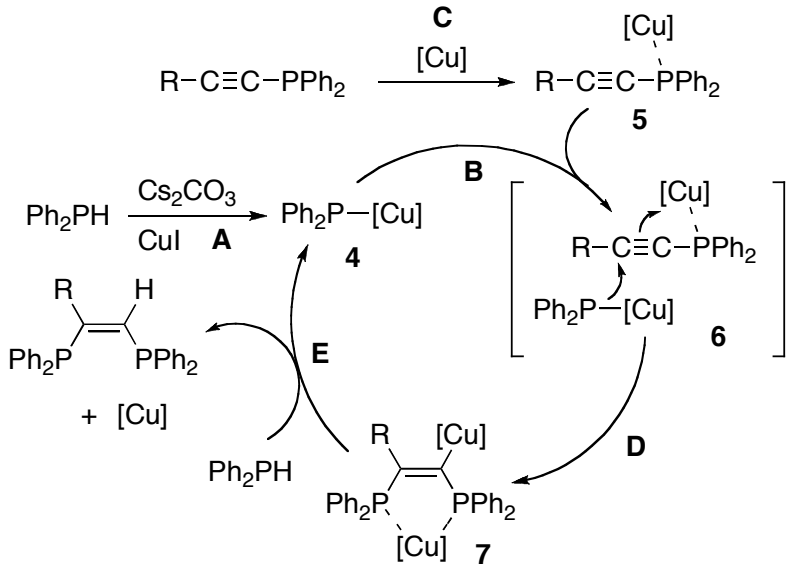




Reaction Mechanism. The mechanism of the phosphination reaction is not clear. Radical inhibitors such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl had little influence on the reaction, which is suggestive of an ionic reaction process. With several experiments, the author is tempted to propose the mechanism outlined in Scheme 2. Deprotonation by Cs_2CO_3 with the aid of copper iodide would provide copper phosphide[14] (step A). As mentioned above, highly basic Cs_2CO_3 is thus essential to abstract the hydrogen of the CuI·$HPPh_2$ complex.[15] The phosphide would then attack 1-alkynylphosphine to form **7** (steps B and D). The alkynylphosphine probably coordinates to copper to be activated in the form of **5**[16] (step C).[17] The activation by copper is indispensable, due to the experimental fact that both 1-octynylphosphine sulfide and oxide resisted the hydrophosphination reaction under the otherwise same reaction conditions. Unlike the insertion of an alkyne to a transition metal–phosphorus bond which proceeds in a *syn* manner, nucleophilic addition to alkyne usually proceeds in an *anti* manner. The latter is the case for the present reaction (step D). Immediate formation of chelating diphosphine skeleton **7** controls the complete stereoselectivity. During the reaction, no *E* isomer was detected, which suggests that it is improbable that initially formed (*E*)-diphosphine isomerizes into its *Z* form in the reaction flask. Protonation of the vinylcopper **7** by $HPPh_2$ affords the product and regenerates the copper

phosphide (step E).

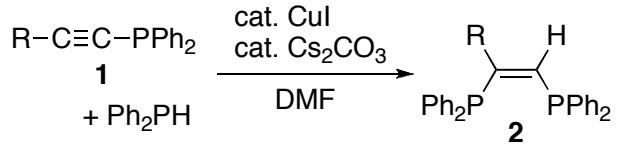
Scheme 2. Plausible Reaction Mechanism



Isolation of Trivalent Phosphines 2. The diphosphines **2** could be handled under air, although gradual oxidation occurred. The isolations of trivalent phosphines **2** are summarized in Table 2. The oxidation led to lower yields of **2**, compared to the yields of sulfides **3** (Table 2 vs Table 1). When the hydrophosphination reaction of **1c** was conducted on a 0.5 mmol scale, **2c** was obtained in 99% NMR yield and 69% isolated yield (Table 2, entry 1). Without special care to avoid oxidation, other phosphines, **2a**, **2d**–**2f**, and **2i**, were isolated in good yields (Table 2, entries 2–6).

The catalytic hydrophosphination reaction was reliable enough to permit a gram-scale synthesis (Table 2, entry 7). The reaction of 1.0 g of **1c** (3.8 mmol) and 0.71 g of diphenylphosphine (3.8 mmol) provided 1.5 g of **2c** (3.3 mmol) in 87% isolated yield after purification on silica gel under ambient atmosphere. The lower isolated yield in the smaller-scale synthesis (Table 2, entry 1) would originate from the formation of a larger proportion of phosphine oxide of **2c**.

Table 2. Isolation of 1,2-Bis(diphenylphosphino)-1-alkenes[a]



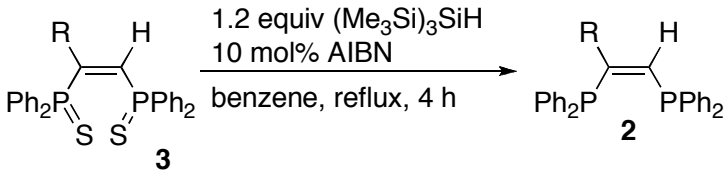
entry	R	CuI /mol%	Cs_2CO_3 /mol%	yield of **2** /%[b]
1[c]	*t*-Bu (**c**)	2	10	69 (99)
2	*n*-C_6H_{13} (**a**)	1	10	71
3	Ph (**d**)	1	10	70
4	4-Ac-C_6H_4 (**e**)	10	20	60
5	3-pyridyl (**f**)	2	10	65
6	PhCH(OH) (**i**)	10	20	51
7[c,d]	*t*-Bu (**c**)	10	20	87

[a] Hydrophosphination conditions: **1** (0.50 mmol), Ph_2PH (0.52 mmol), DMF (3.0 mL), 25 ˚C, 4 h. [b] Isolated yields. NMR yield is in parenthesis. [c] The reaction was performed at 90 ˚C. [d] The reaction was performed with 1.0 g of **1c** (3.8 mmol) and 0.71 g of diphenylphosphine (3.8 mmol).

Radical Reduction of 3 to 2. The author surveyed an efficient method for the reduction of phosphine sulfides **3** to the parent phosphines **2**. Radical desulfidation with tris(trimethylsilyl)silane (TTMSS) proved to be a reliable procedure (Table 3). Although the original report employed 1–3 equimolar amounts of TTMSS,[18] he found that a substoichiometric amount of TTMSS to P=S bond is sufficient. A plausible radical chain mechanism is depicted in Scheme 3. The first equimolar amount of **3** would undergo desulfidation in the reported manner[18] (steps F and G). The silicon-centered radical **10**, which is to be generated by a 1,2-Si shift[19] (step H), would be reactive enough to reduce a P=S moiety. [Bis(trimethylsilylthio)trimethylsilyl]silyl radical (**13**), formed through the second 1,2-shift (step K), seemed unreactive, based on the fact that a smaller amount of TTMSS for the reduction of **3** led to unsatisfactory conversion of **3**. The radical **13** would abstract the hydrogen of TTMSS (step L) to form tris(trimethylsilyl)silyl radical, which completes the radical chain. Purification

on silica gel was quite easy, simply removing less polar silicon residues through a short-path column.

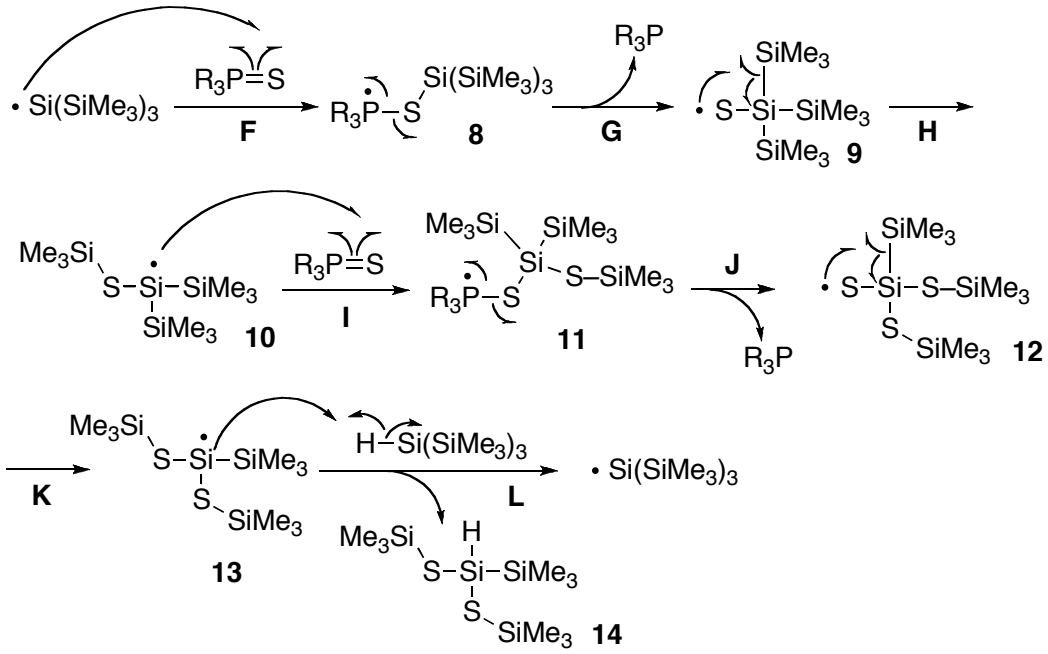
Table 3. Radical Reduction of **3** to **2** by TTMSS[a]



entry	R	isolated yield of **2** /%[b]
1	*t*-Bu (**c**)	89
2	*n*-C_6H_{13} (**a**)	87 (97)[b]
3	Ph (**d**)	78 (94)[b]
4	4-Ac-C_6H_4 (**e**)	63
5	3-pyridyl (**f**)	44
6[c]	3-pyridyl (**f**)	58

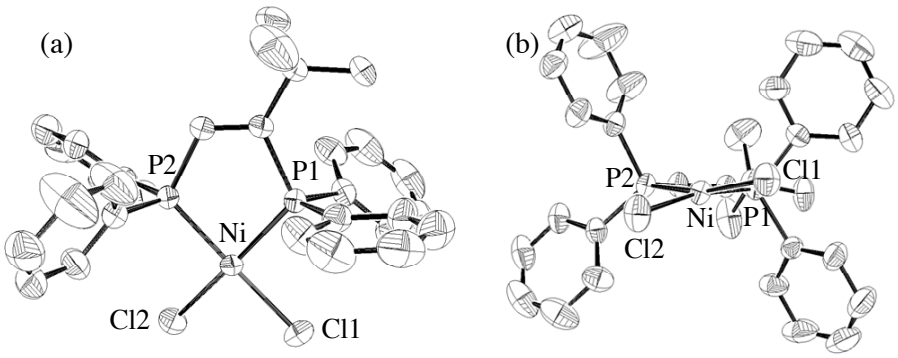
[a] Conditions: **3** (0.25 mmol), TTMSS (0.30 mmol), AIBN (0.025 mmol), benzene (3.0 mL), reflux, 4 h. [b] NMR yields are in parentheses. [c] The reaction was performed with TTMSS (0.60 mmol) for 12 h.

Scheme 3. Mechanism for Desulfidation of **3** with a Substoichiometric Amount of TTMSS



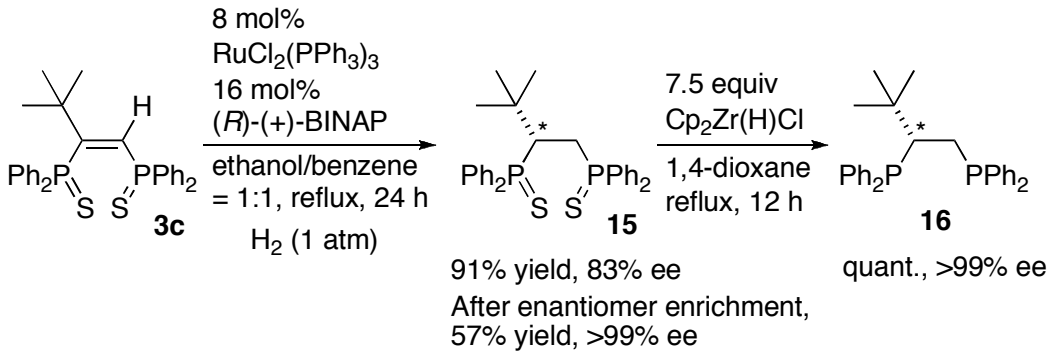
Complexation of $NiCl_2$ with 2c. The *Z* stereochemistry of **2** was also confirmed by X-ray crystallographic analysis of [$NiCl_2$(**2c**)] (Figure 1). Due to the bulky *tert*-butyl group, the atoms, P1, P2, Cl1, and Cl2, coordinating to the nickel are not in one plane (Figure 1b).

Figure 1. ORTEP Drawing of [$NiCl_2$(**2c**)]. (a) Top View. (b) Side View.



Enantioselective Hydrogenation Leading to Chiral Bidentate Phosphine Ligand. Compounds **2** and **3** have carbon–carbon double bonds, which can enjoy further transformations. In light of the importance of chiral bidentate ligands in transition-metal-catalyzed asymmetric synthesis, the author examined enantioselective hydrogenation of **3c** to obtain a new chiral ligand. Enantioselective hydrogenation of **3c** under the catalysis of [$RuCl_2(PPh_3)_3$]/(*R*)-(+)-BINAP provided a *tert*-butyl-substituted chiral diphosphine disulfide **15** in 91% isolated yield with 83% ee (Scheme 4).[20] Recrystallization of the product yielded an enantiomerically pure form of **15** in the supernatant, whereas the crystals were a mixture of the enantiomers. The desulfidation of **15** with a large excess of $Cp_2Zr(H)Cl$[21,22] afforded enantiomerically pure bidentate phosphine **16**. The typical S_N2 phosphination reactions of ditosylates of chiral diols[23] may suffer in the synthesis of phosphines with a sterically congested chiral center. The sequential phosphination/hydrogenation protocol offers an alternative to the conventional approach.

Scheme 4. Synthesis of a New Bidentate Chiral Diphosphine



Conclusion

The author has devised a highly efficient method for the synthesis of (*Z*)-1,2-diphosphino-1-alkenes. The method will create a variety of functionalized bidentate phosphines, which can be applicable to various fields of chemical science. As exemplified by the synthesis of a new chiral bidentate ligand **16**, the (*Z*)-1,2-diphosphino-1-alkene derivatives can be precursors of new phosphorus compounds.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ or C_6D_6. Chemical shifts (δ) are in parts per million relative to chloroform at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.0 ppm for ^{13}C or benzene at 7.15 ppm for ^{1}H and at 128.0 ppm for ^{13}C. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in $CDCl_3$ or C_6D_6 with 85% H_3PO_4 solution as an external standard. NMR yields were determined by fine ^{31}P NMR spectra with $(MeO)_3P=O$ as an internal standard. The first delay of ^{31}P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Determination of enantiomeric excess was performed with Shimadzu LCMS-2010A. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. Sep-Pak® cartridges (silica, long body) for the purification of **16** were purchased from Waters and were used after conditioned with 10 mL of hexane/ethyl acetate (5:1) prior to use.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Diphenylphosphine was purchased from TCI, distilled, and stored under argon. For the preparation of **1**, chlorodiphenylphosphine was purchased from TCI. Chlorodicyclohexylphosphine was a gift from Hokko Chemical Industry Co., Ltd. Starting 1-alkynylphosphines **1** were prepared by the reactions of lithium acetylides with chlorophosphines or by nickel-catalyzed reactions of alkynes with chlorodiphenylphosphine.[10] In general, 1-alkynylphosphines are stable under air. DMF was distilled from calcium hydride and stored under argon. Copper(I) iodide and cesium carbonate were purchased from Wako Pure Chemicals. Tris(triphenylphosphine)ruthenium(II) dichloride was purchased from TCI. Unless otherwise noted, reactions were carried out under argon atmosphere.

Preparation of 1-Alkynylphosphines 1a–1d, 1f, 1j, and 1k (Method A)

Preparation of **1a** is representative. Under an atmosphere of argon, a solution of 1-octyne (1.2 g, 11 mmol) in THF (15 mL) was placed in a 50-mL reaction flask. Butyllithium (6.6 mL, 1.6 M in hexane, 11 mmol) was added to the flask at 0 ˚C. The resulting mixture was stirred for 30 min at the same temperature. Chlorodiphenylphosphine (2.2 g, 10 mmol) was then added at 0 ˚C. After the addition, the reaction mixture was stirred for 1 h at ambient temperature. After water (20 mL) was added, the product was extracted with a hexane/ethyl acetate mixture. Concentration followed by silica gel column purification provided 2.5 g of **1a** (8.5 mmol, 85%) as a yellow oil. It is worth noting that 1-alkynylphosphines are so stable under air that no observable oxidation occurred during the conventional handling. The alkynylphosphines could be stored at least for 6 months in a capped vial.

Preparation of 1-Alkynylphosphines 1e, 1g, and 1h (Method B)

Preparation of **1e** is representative. Nickel acetylacetonate (39 mg, 0.15 mmol) was placed in a 50-mL reaction flask under argon. Toluene (10 mL), *p*-ethynylacetophenone (0.79 g, 5.5 mmol), chlorodiphenylphosphine (1.1 g, 5.0 mmol), and triethylamine (1.5 g, 15 mmol) were sequentially added. The mixture was heated at 80 ˚C for 4 h. After being cooled to room temperature, the mixture was filtered and the filtrate was concentrated. The crude oil obtained was chromatographed on silica gel to yield **1e** in 70% yield (1.1 g, 3.5 mmol).

Preparation of 1i

Crude diphenyl(trimethylsilylethynyl)phosphine was prepared from trimethylsilylacetylene (0.99 mL, 7.0 mmol) by method A. The crude product was dissolved in methanol (10 mL). Potassium carbonate (2.0 g, 14 mmol) was then added. The whole mixture was stirred for 1 h. The product was extracted with a hexane/ethyl acetate mixture. Concentration followed by purification on silica gel provided 1.3 g of ethynyldiphenylphosphine (6.0 mmol, 86%). A part of the ethynylphosphine (0.44 g, 2.1 mmol) was dissolved in 4.0 mL of THF under argon. At 0

˚C, butyllithium (1.3 mL, 1.6 M in hexane, 2.0 mmol) was added dropwise. The mixture was stirred for 30 min. After benzaldehyde (0.20 g, 1.9 mmol) was charged, the mixture was stirred for an additional 1 h at 25 ˚C. The reaction was quenched with 10 mL of water. Extraction, concentration, and purification furnished **1i** in 95% yield (0.57 g, 1.8 mmol).

Typical Procedure for Copper-Catalyzed *anti*-Hydrophosphination of 1-Alkynylphosphines with Diphenylphosphine to Obtain 1,2-Bis(diphenylthiophosphinyl)-1-alkene 3 (Table 1)

Copper(I) iodide (1 mg, 0.005 mmol) and cesium carbonate (16 mg, 0.050 mmol) were placed in a 20-mL reaction flask under argon. DMF (3.0 mL), **1a** (0.15 g, 0.50 mmol), and diphenylphosphine (0.11 g, 0.60 mmol) were sequentially added. The resulting mixture was stirred for 4 h at 25 ˚C. Elemental sulfur (64 mg, 2.0 mmol) was then added and the mixture was stirred for 1 h. Water (10 mL) was added and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded (*Z*)-1,2-bis(diphenylthiophosphinyl)-1-octene (**3a**, 0.24 g, 0.44 mmol, 88%) as a white solid.

Hydrophosphination to Isolate 1,2-Bis(diphenylphosphino)-1-alkene (Table 2, Entries 1–6)

Isolation of **2c** is representative. Copper(I) iodide (1.9 mg, 0.010 mmol) and cesium carbonate (0.016 g, 0.050 mmol) were placed in a 20-mL reaction flask under an atmosphere of argon. DMF (3.0 mL), **1c** (0.13 g, 0.50 mmol), and diphenylphosphine (0.097 g, 0.52 mmol) were sequentially added. The mixture was heated at 90 ˚C for 4 h. After being cooled to room temperature, the mixture was passed through a pad of florisil. The filtrate obtained was evaporated to leave solid. Purification on silica gel provided **2c** (0.16 g, 0.35 mmol) in 69% yield as a white solid. During the process, no deaerated solvents were employed.

Gram-Scale Hydrophosphination to Isolate 2c (Table 2, Entry 7)

The procedure is similar to the smaller-scale reaction. Copper(I) iodide (0.014 g, 0.075

mmol), cesium carbonate (0.12 g, 0.38 mmol), **1c** (1.0 g, 3.8 mmol), and diphenylphosphine (0.71 g, 3.8 mmol) were mixed in DMF (7.5 mL). The whole mixture was heated at 90 ˚C for 4 h. Filtration through a pad of florisil, concentration, and purification afforded 1.5 g of **2c** (3.3 mmol) in 87% yield.

Representative Procedure for TTMSS-Mediated Radical Reduction of 3 to 2 (Table 3)

In a 20-mL reaction flask, **3c** (0.13 g, 0.25 mmol) and AIBN (4.1 mg, 0.025 mmol) were placed under argon. Benzene (3.0 mL) and TTMSS (0.075 g, 0.30 mmol) were added, and the resulting mixture was boiled for 4 h. After cooling, evaporation followed by purification on silica gel furnished 0.10 g of **2c** (0.22 mmol) in 89% yield.

Preparation of [$NiCl_2$(2c)] for X-ray Crystallographic Analysis

Nickel(II) chloride (52 mg, 0.40 mmol) was placed in a 20-mL reaction flask under argon. Ethanol (2.0 mL) was charged to dissolve the nickel salt. Diphosphine **2c** (0.20 g, 0.44 mmol) in ethanol (20 mL) was added. Immediately, orange precipitate appeared. The precipitate was washed with ether, and dried in vacuo. The complex weighed 0.093 g (0.16 mmol, 40%, unoptimized). X-ray quality crystals were grown from acetonitrile. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Center (CCDC 601317).

Ruthenium-Catalyzed Enantioselective Hydrogenation of (*Z*)-3,3-Dimethyl-1,2-bis(diphenylthiophosphinyl)-1-buthene

Tris(triphenylphosphine)ruthenium(II) dichloride (9.6 mg, 0.010 mmol) and (*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-biphenyl ((*R*)-BINAP, 12 mg, 0.020 mmol) were placed in a 20-mL reaction flask under hydrogen. Ethanol (0.50 mL) and benzene (0.50 mL) were added at 25 ˚C. After the mixture was stirred for 10 min, (*Z*)-3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene (**3c**, 65 mg, 0.13 mmol) was added.

The resulting mixture was heated at reflux for 24 h. After the mixture was cooled to room temperature, water (10 mL) was added and the product was extracted with ethyl acetate (10 mL × 3). The organic layer was dried over sodium sulfate and evaporated in vacuo. Purification of the crude solid by gel permeation chromatography provided 3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)butane (**15**, 59 mg, 0.11 mmol) in 91% yield and with 83% ee. Recrystallization from ethanol/benzene yielded crystals. The crystals were a mixture of the enantiomers. Concentration of the supernatant provided an optically pure form of **15** (37 mg, 0.071 mmol, 57%, >99% ee). HPLC conditions: CHIRALCEL AD-H, hexane/2-propanol = 90:10, 1.3 mL/min, retention time = 4.0 min for the major enantiomer; retention time = 5.7 min for the minor enantiomer.

Desulfidation of 15 for Synthesis of New Bidentate Ligand 16

Zirconocene chloride hydride (0.19 g, 0.75 mmol) and **15** (0.052 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. After 1,4-dioxane (3.0 mL) was added, the mixture was stirred for 12 h at reflux. The reaction mixture was directly subjected to evaporation. A mixture of hexane and ethyl acetate (5:1, 10 mL, degassed) was added to dissolve **16**. The supernatant was passed through a silica, long-body Sep-Pak cartridge. The filtrate was concentrated to afford 0.045 g of pure **16** (0.10 mmol, 100%). The absolute configuration of **16** was assigned as *R* by comparing the specific rotations of **16** and of analogous chiral diphosphines.[23c,d]

Characterization Data

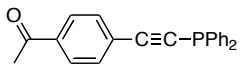
Phosphines **1a**,[24] **1c**,[25] **1d**,[24] and **1k**[26] showed the same spectroscopic data in the literature.

(3-Methyl-1-butynyl)diphenylphosphine (1b)

i-Pr−C≡C−PPh$_2$ IR (neat) 2970, 2930, 2870, 2175, 1683, 1585, 1479, 1436, 1363, 1313, 1267, 1095, 1026, 999, 830, 740, 694, 592 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, *J* = 6.5 Hz, 6H),

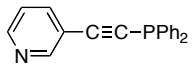
2.85 (dsept, J = 1.5, 6.5 Hz, 1H), 7.32–7.43 (m, 6H), 7.64–7.72 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.95, 22.73, 74.69, 115.66 (d, J = 3.8 Hz), 128.35, 128.54 (d, J = 32.0 Hz), 132.22 (d, J = 21.0 Hz), 137.02 (d, J = 7.1 Hz); ^{31}P NMR ($CDCl_3$) δ –35.13. HRMS (EI^+) (m/z) Observed: 252.1069 (Δ = +0.3 ppm). Calcd for $C_{17}H_{17}P$ [M^+]: 252.1068.

(4-Acetylphenylethynyl)diphenylphosphine (1e)



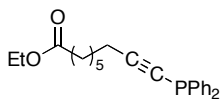
IR (neat) 3054, 1684, 1600, 1557, 1479, 1435, 1402, 1304, 1265, 1178, 1095, 999, 846, 694, 598 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.61 (s, 3H), 7.35–7.41 (m, 6H), 7.63 (d, J = 8.5 Hz, 2H), 7.65–7.70 (m, 4H), 7.93 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.63, 89.91 (d, J = 10.0 Hz), 106.58 (d, J = 3.3 Hz), 127.41 (d, J = 1.1 Hz), 128.20, 128.69 (d, J = 7.6 Hz), 129.19, 131.79 (d, J = 1.5 Hz), 132.62 (d, J = 21.0 Hz), 135.59 (d, J = 5.8 Hz), 136.53, 197.20; ^{31}P NMR ($CDCl_3$) δ –34.75. Found: C, 80.46; H, 5.38%. Calcd for $C_{22}H_{17}OP$: C, 80.48; H, 5.22%. m.p.: 77.0–78.0 °C.

Diphenyl(3-pyridinylethynyl)phosphine (1f)



IR (neat) 3053, 2164, 1584, 1560, 1475, 1435, 1406, 1307, 1185, 1023, 804, 741, 659 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.42 (dd, J = 5.0, 8.0 Hz, 1H), 6.98–7.17 (m, 7H), 7.67–7.75 (m, 4H), 8.27 (d, J = 5.0 Hz , 1H), 8.76 (s, 1H); ^{13}C NMR (C_6D_6) δ 90.53 (d, J = 11.9 Hz), 104.93 (d, J = 3.4 Hz), 119.91 (d, J = 1.5 Hz), 122.77, 129.01 (d, J = 7.6 Hz), 129.39, 133.05 (d, J = 21.0 Hz), 136.33 (d, J = 7.1 Hz), 138.15 (d, J = 1.4 Hz), 149.37, 152.81 (d, J = 1.9 Hz); ^{31}P NMR (C_6D_6) δ –34.52. Found: C, 79.33; H, 4.97%. Calcd for $C_{19}H_{14}NP$: C, 79.43; H, 4.91%.

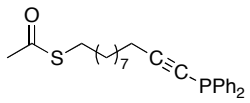
Ethyl 9-diphenylphosphino-8-nonynoate (1g)



IR (neat) 3054, 2936, 2858, 2179, 1733, 1436, 1373, 1181, 1091, 1026, 740, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7.0 Hz, 3H), 1.36 (dd, J = 8.0, 8.0 Hz, 2H), 1.47 (dd, J = 8.0, 8.0 Hz, 2H), 1.58–1.68 (m, 4H), 2.30 (t, J = 7.5 Hz,

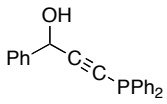
2H), 2.45 (dd, *J* = 7.0, 1.5 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 7.29–7.37 (m, 6H), 7.57–7.63 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.22, 20.26, 24.78, 28.26 (d, *J* = 1.0 Hz), 28.44, 28.53, 34.22, 60.16, 75.84, 110.22 (d, *J* = 3.9 Hz), 128.42 (d, *J* = 7.1 Hz), 128.75, 132.33 (d, *J* = 20.5 Hz), 136.94 (d, *J* = 6.6 Hz), 173.72; ^{31}P NMR ($CDCl_3$) δ –34.51. Found: C, 75.12; H, 7.52%. Calcd for $C_{23}H_{27}O_2P$: C, 75.39; H, 7.43%.

_S_-11-Diphenylphosphino-10-undecynyl ethanethioate (1h)



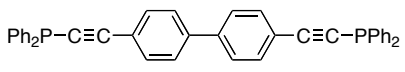
IR (neat) 2928, 2855, 2179, 1733, 1694, 1435, 1353, 1097, 1027, 740, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24–1.48 (m, 10H), 1.56 (dd, *J* = 7.5, 7.5 Hz, 2H), 1.62 (dd, *J* = 7.5, 7.0 Hz, 2H), 2.32 (s, 3H), 2.44 (dd, *J* = 7.0, 1.5 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 7.29–7.37 (m, 6H), 7.58–7.64 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.31, 28.45 (d, *J* =1.1 Hz), 28.73, 28.78, 28.94, 28.99, 29.08, 29.28, 29.43, 30.61, 75.66, 110.46 (d, *J* = 3.9 Hz), 128.41 (d, *J* = 7.1 Hz), 128.72, 132.32 (d, *J* = 20.5 Hz), 136.99 (d, *J* = 6.8 Hz), 196.04; ^{31}P NMR ($CDCl_3$) δ –34.48. Found: C, 72.90; H, 7.90%. Calcd for $C_{25}H_{31}OPS$: C, 73.14; H, 7.61%.

1-Phenyl-3-diphenylphosphino-2-propyn-1-ol (1i)



IR (neat) 3265, 3055, 2857, 1585, 1456, 1436, 1185, 1043, 1027, 986, 916, 741, 695, 511 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.01 (s, 1H), 5.31 (s, 1H), 6.96–7.10 (m, 9H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.64–7.71 (m, 4H); ^{13}C NMR (C_6D_6) δ 65.27, 83.64 (d, *J* =11.5 Hz), 109.30, 126.95, 128.29, 128.66, 128.90 (d, *J* = 7.6 Hz), 129.24, 133.00 (d, *J* = 21.0 Hz), 136.59 (d, *J* = 6.6 Hz), 140.97; ^{31}P NMR (C_6D_6) δ –35.40. Found: C, 79.43; H, 5.54%. Calcd for $C_{21}H_{17}OP$: C, 79.73; H, 5.42%.

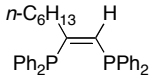
4,4'-Bis(2-diphenylphosphinoethynyl)biphenyl (1j)



IR (nujol) 2924, 2855, 2389, 2161, 1729, 1652, 1456, 1436, 1367, 1026, 843, 821, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ

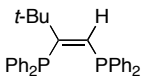
7.34–7.42 (m, 12H), 7.56–7.65 (m, 8H), 7.66–7.72 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 86.99 (d, *J* = 6.6 Hz), 107.42 (d, *J* = 3.8 Hz), 122.12 (d, *J* = 1.6 Hz), 126.89, 128.64 (d, *J* = 7.6 Hz), 129.07, 132.35 (d, *J* = 1.4 Hz), 132.60 (d, *J* = 21.0 Hz), 136.14 (d, *J* = 6.1 Hz), 140.50; ^{31}P NMR ($CDCl_3$) δ –34.72. HRMS (EI$^+$) (*m/z*) Observed: 570.1666 (Δ= 0.0 ppm). Calcd for $C_{40}H_{28}P_2$ [M$^+$]: 570.1666. m.p.: 123.5–125.0 °C.

(*Z*)-1,2-Bis(diphenylphosphino)-1-octene (2a)



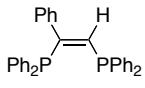
IR (neat) 3052, 3000, 2926, 2855, 1951, 1884, 1585, 1480, 1436, 1378, 1093, 839, 741, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, *J* = 7.5 Hz, 3H), 1.20–1.30 (m, 8H), 2.08–2.15 (m, 2H), 7.00 (d, *J* = 33.5 Hz, 1H), 7.24–7.40 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.42, 28.81, 28.83, 31.40, 36.86, 128.10, 128.13 (d, *J* = 7.1 Hz), 128.18, 128.24 (d, *J* = 6.6 Hz), 132.78 (d, *J* = 18.6 Hz), 133.33 (d, *J* = 19.0 Hz), 136.40 (dd, *J* = 5.3, 12.9 Hz), 139.57 (dd, *J* = 4.3, 12.8 Hz), 141.37 (dd, *J* = 7.6, 35.8 Hz), 156.12 (dd, *J* = 18.6, 25.8 Hz); ^{31}P NMR ($CDCl_3$) δ –27.48 (d, *J* = 161.1 Hz), –9.67 (d, *J* = 161.1 Hz). Found: C, 80.11; H, 7.10%. Calcd for $C_{32}H_{34}P_2$: C, 79.98; H, 7.13%.

(*Z*)-3,3-Dimethyl-1,2-bis(diphenylphosphino)-1-butene (2c)



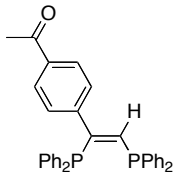
IR (nujol) 2924, 2854, 1700, 1559, 1456, 1432, 1377, 1356, 1230, 1028, 846, 736, 692 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.26 (s, 9H), 6.94–7.07 (m, 12H), 7.20–7.27 (m, 4H), 7.31 (dd, *J* = 16.0, 3.5 Hz, 1H), 7.62–7.68 (m, 4H); ^{13}C NMR (C_6D_6) δ 30.30 (d, *J* = 9.5 Hz), 41.32 (dd, *J* = 27.4, 6.9 Hz), 127.95, 128.32 (d, *J* = 6.3 Hz), 128.34, 128.44 (d, *J* = 5.8 Hz), 133.02 (d, *J* = 19.0 Hz), 133.44 (dd, *J* = 18.9, 3.5 Hz), 137.18 (dd, *J* = 14.1, 4.1 Hz), 139.55 (dd, *J* = 14.1, 1.2 Hz), 140.82 (d, *J* = 14.8 Hz), 165.39 (dd, *J* = 29.1, 22.9 Hz); ^{31}P NMR (C_6D_6) δ –32.26 (d, *J* = 29.3 Hz), –12.35 (d, *J* = 29.3 Hz). Found: C, 79.39; H, 6.65%. Calcd for $C_{30}H_{30}P_2$: C, 79.63; H, 6.68%. m.p.: 85.5–87.0 °C.

(*Z*)-1-Phenyl-1,2-bis(diphenylphosphino)ethene (2d)



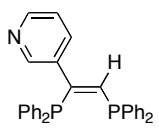
IR (neat) 3052, 3000, 2925, 2855, 1951, 1884, 1811, 1584, 1480, 1307, 1093, 1069, 1026, 999, 738, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.86–6.90 (m, 2H), 6.96–7.05 (m, 3H), 7.10–7.20 (m, 6H), 7.21–7.30 (m, 11H), 7.35–7.41 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 126.87, 127.38, 127.82, 128.01 (d, *J* = 6.6 Hz), 128.10, 128.34, 128.37 (d, *J* = 6.6 Hz), 132.97 (d, *J* = 19.0 Hz), 133.24 (d, *J* = 19.1 Hz), 135.80 (dd, *J* = 5.1, 12.0 Hz), 139.04 (dd, *J* = 4.9, 10.5 Hz), 142.35 (dd, *J* = 2.4, 8.1 Hz), 146.03 (dd, *J* = 11.5, 37.8 Hz), 155.71 (dd, *J* = 23.4, 27.1 Hz) ; ^{31}P NMR ($CDCl_3$) δ –27.19 (d, *J* = 144.8 Hz), –6.24 (d, *J* = 144.8 Hz). Found: C, 81.19; H, 5.72%. Calcd for $C_{32}H_{26}P_2$: C, 81.34; H, 5.55%.

(*Z*)-2-(4-Acetylphenyl)-1,2-bis(diphenylphosphino)ethene (2e)



IR (nujol) 2925, 2855, 2723, 1738, 1673, 1598, 1456, 1377, 1265, 1160, 740, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3H), 6.97 (d, *J* = 8.5 Hz, 2H), 7.12–7.26 (m, 10H), 7.27–7.36 (m, 7H), 7.37–7.44 (m, 4H), 7.61 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.52, 127.54, 127.99, 128.17 (d, *J* = 6.8 Hz), 128.41 (d, *J* = 7.6 Hz), 128.49, 128.51, 132.98 (d, *J* = 16.3 Hz), 133.13 (d, *J* = 16.8 Hz), 135.20 (dd, *J* = 5.3, 12.9 Hz), 135.27, 138.67 (dd, *J* = 4.8, 10.5 Hz), 147.23 (dd, *J* = 3.3, 8.5 Hz), 147.69 (dd, *J* = 13.4, 38.1 Hz), 154.57 (dd, *J* = 24.8, 27.8 Hz), 197.62; ^{31}P NMR ($CDCl_3$) δ –26.54 (d, *J* = 141.5 Hz), –6.54 (d, *J* = 141.5 Hz). Found: C, 79.09; H, 5.53%. Calcd for $C_{34}H_{28}OP_2$: C, 79.37; H, 5.48%. m.p.: 160.0–162.5° C.

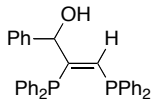
(*Z*)-2-(3-Pyridyl)-1,2-bis(diphenylphosphino)ethene (2f)



IR (nujol) 3051, 2925, 2855, 1959, 1882, 1814, 1584, 1568, 1471, 1436, 1407, 1377, 1184, 1094, 1025, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.86 (dd, *J* = 5.0, 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.12–7.25 (m, 10H), 7.26–7.36 (m, 7H), 7.37–7.46 (m, 4H), 8.22 (s, 1H), 8.26 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 121.99, 128.21 (d, *J* = 6.3 Hz), 128.40 (2C), 128.47 (d, *J* = 4.9 Hz), 132.91 (d, *J* = 19.1 Hz), 133.06 (d, *J* = 19.1 Hz), 134.67,

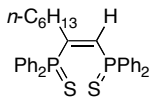
135.00 (dd, *J* = 5.3, 13.0 Hz), 138.03 (dd, *J* = 3.4, 6.1 Hz), 138.47 (dd, *J* = 4.8, 10.5 Hz), 147.86, 148.22 (dd, *J* = 13.4, 37.3 Hz), 148.26, 151.98 (dd, *J* = 24.9, 28.6 Hz); ^{31}P NMR ($CDCl_3$) δ –26.51 (d, *J* = 140.0 Hz), –6.75 (d, *J* = 140.0 Hz). Found: C, 78.51; H, 5.46%. Calcd for $C_{31}H_{25}NP_2$: C, 78.64; H, 5.32%. m.p.: 111.0–112.5° C.

(*Z*)-1-Phenyl-2,3-bis(diphenylphosphino)-2-propen-1-ol (2i)



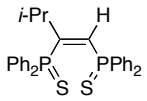
IR (nujol) 3446, 3047, 2953, 2923, 2854, 1652, 1569, 1456, 1436, 1377, 1306, 1177, 1070, 989, 913, 857 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 1H), 5.23 (s, 1H), 6.89–6.94 (m, 2H), 7.05–7.19 (m, 8H), 7.20–7.33 (m, 13H), 7.34–7.53 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 76.12 (dd, *J* = 1.8, 7.8 Hz), 127.03, 127.61, 128.03, 128.12 (d, *J* = 6.6 Hz), 128.23, 128.28, 128.32 (d, *J* = 6.3 Hz), 128.37 (d, *J* = 7.6 Hz), 128.43, 128.46 (d, *J* = 7.3 Hz), 128.56, 132.52 (d, *J* = 18.6 Hz), 133.28 (d, *J* = 19.0 Hz), 133.39 (d, *J* = 19.0 Hz), 134.27 (d, *J* = 20.5 Hz), 135.03 (dd, *J* = 7.5, 13.0 Hz), 135.56 (dd, *J* = 2.6, 10.5 Hz), 138.31 (dd, *J* =3.9, 10.5 Hz), 139.38 (dd, *J* = 4.6, 10.5 Hz), 141.28, 142.22 (dd, *J* = 10.0, 32.4 Hz), 155.57 (dd, *J* = 22.4, 25.8 Hz); ^{31}P NMR ($CDCl_3$) δ –29.55 (d, *J* = 143.2 Hz), –13.18 (d, *J* = 143.2 Hz). Found: C, 78.74; H, 5.58%. Calcd for $C_{33}H_{28}OP_2$: C, 78.88; H, 5.62%. m.p.: 106.0–109.0° C.

(*Z*)-1,2-Bis(diphenylthiophosphinyl)-1-octene (3a)



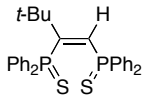
IR (nujol) 2923, 2854, 2392, 1456, 1436, 1377, 1313, 1101, 1030, 818, 747, 707, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, *J* = 7.5 Hz, 3H), 1.07–1.22 (m, 6H), 1.54 (tt, *J* = 8.0, 8.0 Hz, 2H), 2.38 (dt, *J* = 12.0, 8.0 Hz, 2H), 6.94 (dd, *J* = 41.5, 13.0 Hz, 1H), 7.22–7.40 (m, 12H), 7.65–7.80 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.44, 28.74, 30.63 (d, *J* = 3.8 Hz), 31.30, 39.69 (dd, *J* = 14.9, 12.9 Hz), 128.20 (d, *J* = 12.9 Hz), 128 .35 (d, *J* = 12.9 Hz), 130.99 (d, *J* = 2.9 Hz), 131.18 (d, *J* = 10.5 Hz), 131.25 (d, *J* = 83.0 Hz), 131.28 (d, *J* = 2.9 Hz), 132.33 (d, *J* = 10.9 Hz), 133.59 (d, *J* = 86.4 Hz), 134.66 (dd, *J* = 81.5, 7.6 Hz), 152.21 (dd, *J* = 67.9, 3.3 Hz); ^{31}P NMR ($CDCl_3$) δ 29.28 (d, *J* = 16.3 Hz), 39.58 (d, *J* = 16.3 Hz). Found: C, 70.48; H, 6.32%. Calcd for $C_{32}H_{34}P_2S_2$: C, 70.56; H, 6.29%. m.p.: 119.0–120.5 °C.

(*Z*)-3-Methyl-1,2-bis(diphenylthiophosphinyl)-1-butene (3b)



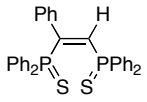
IR (nujol) 2924, 2855, 2391, 1457, 1436, 1381, 1101, 998, 832, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (d, *J* = 7.0 Hz, 6H), 2.88 (dsept, *J* = 3.5, 6.5 Hz, 1H), 6.98 (dd, *J* = 12.0, 45.0 Hz, 1H), 7.20–7.41 (m, 12H), 7.62–7.70 (m, 4H), 7.76–7.83 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 25.40 (dd, *J* = 3.4, 0.90 Hz), 35.44 (dd, *J* = 13.8, 14.0 Hz), 128.09 (d, *J* = 12.9 Hz), 128.48 (d, *J* = 12.5 Hz), 130.72 (d, *J* = 83.1 Hz), 130.89 (d, *J* = 10.5 Hz), 130.99 (d, *J* = 2.9 Hz), 131.32 (d, *J* = 2.9 Hz), 132.59 (d, *J* = 10.5 Hz), 132.70 (dd, *J* = 7.3, 83.6 Hz), 133.93 (d, *J* = 86.9 Hz), 159.53 (dd, *J* = 4.3, 68.3 Hz); ^{31}P NMR ($CDCl_3$) δ 28.93 (d, *J* = 5.7 Hz), 41.58 (d, *J* = 5.7 Hz). Found: C, 69.11; H, 5.56%. Calcd for $C_{29}H_{28}P_2S_2$: C, 69.30; H, 5.61%. m.p.: 149.0–150.5 °C.

(*Z*)-3,3-Dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene (3c)



IR (nujol) 2925, 2855, 1700, 1653, 1457, 1437, 1097 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 9H), 7.14–7.24 (m, 5H), 7.27–7.40 (m, 8H), 7.60–7.68 (m, 4H), 7.70–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 32.67 (d, *J* = 2.9 Hz), 42.98 (dd, *J* = 10.5, 13.4 Hz), 127.55 (d, *J* = 12.4 Hz), 128.31 (d, *J* = 13.0 Hz), 130.87 (d, *J* = 2.5 Hz), 130.90 (d, *J* = 10.5 Hz), 131.01 (d, *J* = 2.9 Hz), 132.71 (d, *J* = 11.0 Hz), 132.87 (d, *J* = 82.0 Hz), 134.25 (d, *J* = 86.9 Hz), 135.71 (dd, *J* = 7.3, 80.3 Hz), 159.52 (dd, *J* = 6.6, 61.5 Hz); ^{31}P NMR ($CDCl_3$) δ 31.37 (d, *J* = 19.4 Hz), 36.64 (d, *J* = 19.4 Hz). Found: C, 69.66; H, 5.83%. Calcd for $C_{30}H_{30}P_2S_2$: C, 69.74; H, 5.85%. m.p.: 165.0–166.0 °C.

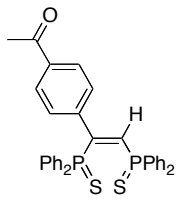
(*Z*)-1-Phenyl-1,2-bis(diphenylthiophosphinyl)ethene (3d)



IR (nujol) 2924, 2855, 2390, 2349, 1507, 1457, 1437, 645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.92–7.20 (m, 8H), 7.22–7.43 (m, 10H), 7.62–7.70 (m, 4H), 7.73–7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 127.82, 127.96 (d, *J* = 1.5 Hz), 128.07 (d, *J* = 12.9 Hz), 128.21 (d, *J* = 3.8 Hz), 128.34 (d, *J* = 12.9 Hz), 130.93 (d, *J* = 2.9 Hz), 131.15 (d, *J* = 3.4 Hz), 131.57 (d, *J* = 10.5 Hz), 131.72 (d, *J* = 84.9 Hz), 131.94 (d, *J* = 10.5 Hz), 132.63 (d, *J* = 86.4 Hz), 138.97

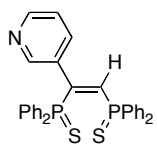
(dd, *J* = 8.1, 74.5 Hz), 141.87 (dd, *J* = 10.0, 16.6 Hz), 150.76 (dd, *J* = 1.8, 70.0 Hz); ^{31}P NMR ($CDCl_3$) δ 30.12 (d, *J* = 11.4 Hz), 35.71 (d, *J* = 11.4 Hz). Found: C, 71.38; H, 4.72%. Calcd for $C_{32}H_{26}P_2S_2$: C, 71.62; H, 4.88%. m.p.: 179.5–181.0 ˚C.

(*Z*)-2-(4-Acetylphenyl)-1,2-bis(diphenylthiophosphinyl)ethene (3e)



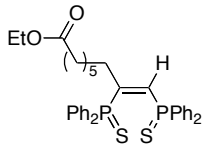
IR (nujol) 2924, 2854, 1734, 1684, 1601, 1456, 1438, 1386, 1265, 1098, 919 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 3H), 7.06 (dd, *J* = 12.0, 38.0 Hz, 1H), 7.12–7.20 (m, 4H), 7.23–7.42 (m, 8H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.63–7.80 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.57, 127.80, 128.20 (d, *J* = 12.9 Hz), 128.41 (d, *J* = 12.9 Hz), 128.54 (d, *J* = 3.4 Hz), 131.16 (d, *J* = 85.4 Hz), 131.18 (d, *J* = 2.9 Hz), 131.27 (d, *J* = 2.8 Hz), 131.48 (d, *J* = 11.0 Hz), 131.90 (d, *J* = 10.5 Hz), 132.28 (d, *J* = 85.4 Hz), 136.09 (d, *J* = 1.5 Hz), 139.61 (dd, *J* = 7.6, 74.4 Hz), 146.48 (dd, *J* = 10.5, 16.6 Hz), 149.66 (d, *J* = 69.8 Hz), 197.33; ^{31}P NMR ($CDCl_3$) δ 30.28 (d, *J* = 11.4 Hz), 35.44 (d, *J* = 11.4 Hz). Found: C, 70.60; H, 4.70%. Calcd for $C_{34}H_{28}OP_2S_2$: C, 70.57; H, 4.88%. m.p.: 175.5–177.0 ˚C.

(*Z*)-2-(3-Pyridinyl)-1,2-bis(diphenylthiophosphinyl)ethene (3f)



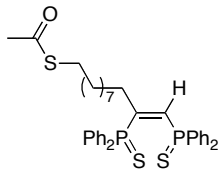
IR (nujol) 2924, 2854, 2389, 1734, 1653, 1558, 1457, 1437, 687, 651, 587 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.32 (dd, *J* = 5.0, 8.0 Hz, 1H), 6.74–6.95 (m, 12H), 7.08 (dd, *J* = 11.5, 38.0 Hz, 1H) 7.66–7.71 (m, 1H), 7.77–7.85 (m, 4H), 7.88–7.97 (m, 4H), 8.15 (d, *J* = 4.0 Hz, 1H), 8.93 (s, 1H); ^{13}C NMR (C_6D_6) δ 122.14, 128.42 (d, *J* = 12.5 Hz), 128.56 (d, *J* = 12.8 Hz), 131.14 (d, *J* = 2.9 Hz), 131.16 (d, *J* = 2.9 Hz), 131.82 (d, *J* = 10.9 Hz), 131.90 (d, *J* = 83.0 Hz), 132.28 (d, *J* = 10.5 Hz), 133.22 (d, *J* = 86.4 Hz), 135.06 (d, *J* = 2.9 Hz), 138.25 (dd, *J* = 10.5, 16.8 Hz), 140.38 (dd, *J* = 8.1, 66.4 Hz), 147.13 (d, *J* = 71.1 Hz), 149.30 (d, *J* = 3.8 Hz), 149.40 (d, *J* = 1.4 Hz); ^{31}P NMR (C_6D_6) δ 30.36 (d, *J* = 11.4 Hz), 35.66 (d, *J* = 11.4 Hz). Found: C, 68.97; H, 4.78%. Calcd for $C_{31}H_{25}NP_2S_2$: C, 69.26; H, 4.69%. m.p.: 182.0–183.0 ˚C.

Ethyl (*Z*)-8,9-bis(diphenylthiophosphinyl)-8-nonenoate (3g)



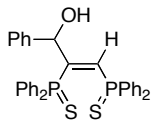
IR (nujol) 2924, 2855, 1734, 1700, 1653, 1457, 1437, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12–1.21 (m, 4H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.46–1.60 (m, 4H), 2.21 (t, *J* = 7.5 Hz, 2H), 2.38 (dt, *J* = 11.5, 8.0 Hz, 2H), 4.11 (q, *J* = 7.5 Hz, 2H), 6.94 (dd, *J* = 13.0, 41.5 Hz, 1H), 7.22–7.40 (m, 12H), 7.66–7.78 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 14.15, 24.59, 28.48, 28.61, 30.43 (d, *J* = 2.9 Hz), 34.04, 39.52 (dd, *J* = 12.9, 14.9 Hz), 60.06, 128.09 (d, *J* = 12.4 Hz), 128.26 (d, *J* = 12.4 Hz), 130.92 (d, *J* = 2.9 Hz), 131.04 (d, *J* = 10.5 Hz), 131.10 (d, *J* = 83.5 Hz), 131.21 (d, *J* = 2.9 Hz), 132.22 (d, *J* = 11.0 Hz), 133.45 (d, *J* = 86.4 Hz), 134.71 (dd, *J* = 7.1, 81.1 Hz), 151.95 (dd, *J* = 2.9, 68.3 Hz), 173.52; ^{31}P NMR ($CDCl_3$) δ 29.30 (d, *J* = 17.9 Hz), 39.67 (d, *J* = 17.9 Hz). Found: C, 67.96; H, 6.32%. Calcd for $C_{35}H_{38}O_2P_2S_2$: C, 68.16; H, 6.21%. m.p.: 44.0–46.5 °C.

***S*-(*Z*)-10,11-Bis(diphenylthiophosphinyl)-10-undecenyl ethanethioate (3h)**



IR (nujol) 2924, 2854, 1686, 1588, 1462, 1438, 1378, 1100, 1027, 749, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07–1.35 (m, 10H), 1.50–1.59 (m, 4H), 2.32 (s, 3H), 2.39 (dt, *J* = 11.0, 8.0 Hz, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 6.93 (dd, *J* = 12.5, 42.0 Hz, 1H), 7.21–7.42 (m, 12H), 7.65–7.82 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 28.54, 28.78, 28.84, 28.86, 28.95, 29.05, 29.31, 30.50, 30.53, 39.54 (dd, *J* = 12.9, 14.9 Hz), 128.07 (d, *J* = 12.9 Hz), 128.22 (d, *J* = 12.4 Hz), 130.87 (d, *J* = 2.9 Hz), 131.03 (d, *J* = 10.5 Hz), 131.13 (d, *J* = 83.0 Hz), 131.17 (d, *J* = 2.9 Hz), 132.18 (d, *J* = 10.5 Hz), 133.46 (d, *J* = 86.4 Hz), 134.58 (dd, *J* = 7.1, 81.1 Hz), 152.05 (dd, *J* = 2.9, 67.8 Hz), 195.86; ^{31}P NMR ($CDCl_3$) δ 29.38 (d, *J* = 16.3 Hz), 39.68 (d, *J* = 16.3 Hz). Found: C, 67.34; H, 6.62%. Calcd for $C_{37}H_{42}OP_2S_3$: C, 67.24; H, 6.41%. m.p.: 61.0–63.0 °C.

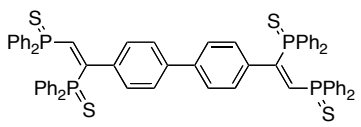
(*Z*)-1-Phenyl-2,3-bis(diphenylthiophosphinyl)-2-propen-1-ol (3i)



IR (nujol) 3392, 2924, 2855, 1700, 1451, 1439, 1378, 1097, 841, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 1H), 5.78 (dd, *J* = 3.0, 8.5 Hz, 1H), 7.01–7.07 (m, 2H),

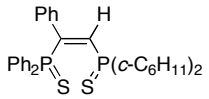
7.17–7.45 (m, 20H), 7.54–7.61 (m, 2H), 7.97–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 75.18 (dd, *J* = 14.8, 17.3 Hz), 126.71, 127.75 (d, *J* = 13.0 Hz), 127.95, 128.41 (d, *J* = 12.4 Hz), 128.50, 128.53 (d, *J* = 13.1 Hz), 128.55 (d, *J* = 12.5 Hz), 129.33 (d, *J* = 53.9 Hz), 130.01 (d, *J* = 53.0 Hz), 130.38 (d, *J* = 10.1 Hz), 130.90 (d, *J* = 3.3 Hz), 131.06 (d, *J* = 11.0 Hz), 131.29 (d, *J* = 2.9 Hz), 131.56 (d, *J* = 3.4 Hz), 132.08 (d, *J* = 2.9 Hz), 132.30 (d, *J* = 85.9 Hz), 132.77 (d, *J* = 10.9 Hz), 133.51 (d, *J* = 11.5 Hz), 135.49 (d, *J* = 88.3 Hz), 137.77 (dd, *J* = 5.8, 80.3 Hz), 139.91 (d, *J* = 6.3 Hz), 154.89 (dd, *J* = 2.5, 68.6 Hz); ^{31}P NMR ($CDCl_3$) δ 27.62 (d, *J* = 16.3 Hz), 40.41 (d, *J* = 16.3 Hz). Found: C, 70.04; H, 4.89%. Calcd for $C_{33}H_{28}OP_2S_2$: C, 69.95; H, 4.98%. m.p.: 207.2–208.5 °C.

(*Z*),(*Z*)-4,4'-Bis[1,2-bis(diphenylthiophosphinyl)ethenyl]biphenyl (3j)



IR (nujol) 2925, 2855, 1456, 1436, 1377, 1256, 1099, 999, 826, 786, 743, 707, 644, 614, 609 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.05–7.50 (m, 34H), 7.64–7.84 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 126.12, 128.04 (d, *J* = 12.5 Hz), 128.33 (d, *J* = 12.9 Hz), 128.72 (d, *J* = 3.3 Hz), 130.96 (d, *J* = 2.4 Hz), 131.15 (d, *J* = 2.4 Hz), 131.41 (d, *J* = 10.5 Hz), 131.48 (d, *J* = 84.5 Hz), 131.94 (d, *J* = 10.5 Hz), 132.61 (d, *J* = 86.4 Hz), 138.86 (dd, *J* = 8.6, 74.5 Hz), 139.51, 141.14 (dd, *J* = 10.5, 16.8 Hz), 150.39 (d, *J* = 69.8 Hz); ^{31}P NMR ($CDCl_3$) δ 30.03 (d, *J* = 13.0 Hz), 35.93 (d, *J* = 13.0 Hz). HRMS (FAB$^+$, Matrix: NBA/$CHCl_3$) (*m/z*) Observed: 1071.1827 (Δ = +0.3 ppm). Calcd for $C_{64}H_{50}P_4S_4$ [MH$^+$]: 1071.1824. m.p.: 217.5–219.5 °C.

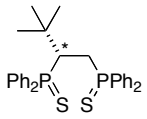
(*Z*)-1-Phenyl-2-dicyclohexylthiophosphinyl-1-diphenylthiophosphinylethene (3k)



IR (nujol) 2923, 2852, 1436, 1377, 1091, 1000, 881, 868, 796, 764, 749, 696, 622, 519 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02–1.34 (m, 6H), 1.42–1.57 (m, 4H), 1.60–1.94 (m, 10H), 2.52–2.63 (m, 2H), 6.66 (dd, *J* = 12.0, 40.5 Hz, 1H), 6.93–7.08 (m, 5H), 7.25–7.32 (m, 4H), 7.33–7.40 (m, 2H), 7.68–7.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 25.65 (d, *J* = 1.9 Hz), 26.23 (d, *J* = 13.8 Hz), 26.31 (d, *J* = 13.8 Hz), 26.66 (d, *J* = 1.9

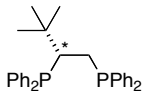
Hz), 26.98 (d, *J* = 3.3 Hz), 39.61 (d, *J* = 49.6 Hz), 127.54 (d, *J* = 1.5 Hz), 127.76, 127.97 (d, *J* = 4.6 Hz), 128.00 (d, *J* = 12.9 Hz), 131.20 (d, *J* = 2.9 Hz), 131.54 (d, *J* = 10.5 Hz), 133.48 (d, *J* = 85.9 Hz), 142.50 (dd, *J* = 10.5, 14.4 Hz), 142.80 (dd, *J* = 9.1, 54.9 Hz), 153.46 (dd, *J* = 3.3, 68.3 Hz); ^{31}P NMR ($CDCl_3$) δ 36.08 (d, *J* = 11.3 Hz), 52.21 (d, *J* = 11.3 Hz). Found: C, 70.03; H, 7.03%. Calcd for $C_{32}H_{38}P_2S_2$: C, 70.04; H, 6.98%. m.p.: 205.0–206.5 °C.

(*R*)-3,3-Dimethyl-1,2-bis(diphenylthiophosphinyl)butane (15)



IR (nujol) 2925, 2854, 1617, 1464, 1432, 1377, 1309, 1097, 1025, 999, 820, 715, 697, 627, 539 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 9H), 2.74–2.96 (m, 2H), 4.28–4.46 (m, 1H), 7.04–7.30 (m, 8H), 7.40–7.52 (m, 6H), 7.84–7.94 (m, 2H), 8.18–8.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 27.77 (dd, *J* = 4.8, 49.6 Hz), 30.40 (d, *J* = 6.3 Hz), 36.26, 42.64 (dd, *J* = 2.8, 50.6 Hz), 128.21 (d, *J* = 12.4 Hz, 2C), 128.35 (d, *J* = 11.9 Hz), 128.52 (d, *J* = 12.5 Hz), 130.13 (d, *J* = 10.0 Hz), 130.64 (d, *J* = 2.8 Hz), 130.83 (d, *J* = 2.9 Hz), 131.12 (d, *J* = 10.0 Hz), 131.16 (d, *J* = 3.9 Hz), 131.32(d, *J* = 2.9 Hz), 131.68 (d, *J* = 9.6 Hz), 132.25 (d, *J* = 76.4 Hz) , 132.27 (d, *J* = 9.0 Hz), 133.47 (d, *J* = 78.8 Hz), 134.45 (d, *J* = 57.8 Hz), 135.08 (d, *J* = 65.9 Hz); ^{31}P NMR ($CDCl_3$) δ 45.23 (d, *J* = 37.4 Hz), 48.72 (d, *J* = 37.4 Hz). HRMS (EI$^+$) (*m/z*) Observed: 518.1425 (Δ = +0.9 ppm). Calcd for $C_{30}H_{32}P_2S_2$ [M$^+$]: 518.1421. m.p.: 208.0–209.5 °C. $[\alpha]_D^{25}$ = –30 (*c* 0.61, $CHCl_3$). The *R* configuration was deduced from the assignment of **16**.

(*R*)-3,3-Dimethyl-1,2-bis(diphenylphosphino)butane (16)



IR (neat) 3052, 2959, 2863, 2321, 1734, 1584, 1476, 1434, 1392, 1363, 1261, 1094, 801, 740, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9H), 1.87–1.97 (m, 1H), 2.21–2.31 (m, 2H), 6.80–6.87 (m, 2H), 7.13–7.42 (m, 12H), 7.44–7.55 (m, 4H), 7.60–7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.92 (d, *J* = 16.1 Hz), 28.76 (d, *J* = 12.4 Hz), 35.49 (dd, *J* = 6.3, 22.5 Hz), 43.72 (dd, *J* = 14.3, 24.3 Hz), 127.65, 127.82 (d, *J* = 7.6 Hz), 127.97 (d, *J* = 5.3 Hz), 128.27, 128.30 (d, *J* = 7.3 Hz), 128.32 (d, *J* = 7.1 Hz), 128.45, 129.11, 132.04 (d, *J* =

17.3 Hz), 134.00 (dd, J = 2.9, 20.6 Hz), 134.43 (d, J = 20.5 Hz), 135.73 (dd, J = 3.4, 21.5 Hz), 137.02 (d, J = 18.6 Hz), 138.00 (d, J = 16.8 Hz), 138.30 (d, J = 11.9 Hz), 139.80 (d, J = 16.3 Hz); ^{31}P NMR ($CDCl_3$) δ –15.81, –4.92. $[\alpha]_D^{25}$ = +15 (*c* 0.063, $CHCl_3$). The *R* configuration was assigned by comparing the specific rotations of **16**, (*R*)-1,2-bis(diphenylthiophosphinyl)propane {$[\alpha]_D^{25}$ = +186 (*c* 1, acetone)},[23c] and (*R*)-[1,2-bis(diphenylthiophosphinyl)ethyl]-cyclohexane {$[\alpha]_D^{25}$ = +103.3 (*c* 1, THF)}.[23d]

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(15) One singlet signal appeared at δ = –41.6 ppm in the ^{31}P NMR spectrum of

diphenylphosphine in DMF. The addition of a stoichiometric amount of CuI to the DMF solution resulted in the formation of a clear solution and in broadening the signal with unambiguous splitting. Upon further addition of a stoichiometric amount of cesium carbonate, the signal disappeared and no new discrete signals were observed. These facts indicate that the copper-phosphorus bond of the complex [CuI•$HPPh_2$] would be labile and that many sorts of copper-phosphide species might be formed upon the addition of cesium carbonate.

(16) There can be an interaction between the copper and the acetylenic part of **5**.

(17) One singlet signal appeared at δ = –34.7 ppm in the ^{31}P NMR spectrum of **1a** in DMF. The addition of a stoichiometric amount of CuI to the DMF solution furnished a clear homogeneous solution, which exhibited a broad and highly splitting signal at the same chemical shift. The dissolution of CuI indicates the formation of the complex [CuI•**1a**]. The NMR experiments suggest that the complex would not be robust.

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(22) The radical desulfidation of **15** with TTMSS (1.2 equiv to **15**) was also successful. However, after several attempts, separation of **15** and silicon-containing residue proved to be problematic in the author's hands. Small amounts of the corresponding monooxides of **15** were generated during careful chromatographic purification on silica gel for isolation of **15**. Purification using a solid phase technique resulted in unsatisfactory separation of **15** and the silicon-containing residue. The author expects that, if the TTMSS-mediated reduction and

purification of **15** were performed in a glove box filled with inert gas, one could isolate **15** in excellent yield.

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Chapter 2

Palladium-Catalyzed *anti*-Hydrothiolation of 1-Alkynylphosphines

Treatment of 1-alkynylphosphine with thiol in the presence of a catalytic amount of palladium acetate results in regio- and stereoselective *anti*-hydrothiolation, yielding the corresponding (*Z*)-1-phosphino-2-thio-1-alkene.

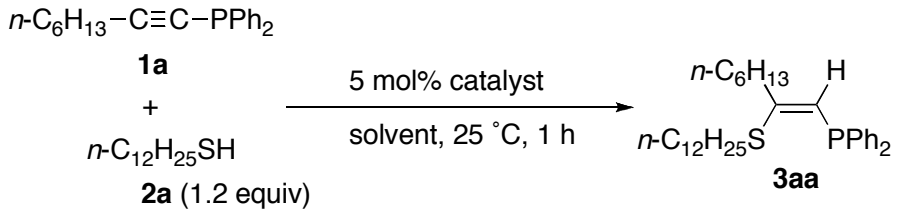
Introduction

Metal-catalyzed addition of thiols to alkynes (hydrothiolation) is an important reaction for synthesizing 1-alkenylsulfides under mild conditions.[1,2] In this chapter, the author discloses that hydrothiolation of 1-alkynylphosphines proceeds smoothly under palladium catalysis. In general, transition-metal-catalyzed hydrothiolation proceeds in a *syn* fashion.[1,2f,3] In contrast, the present reaction represents a rare example of highly selective *anti*-hydrothiolation.[2d,g,4] The products, (*Z*)-1-phosphino-2-thio-1-alkenes, are a new class of heteroatom-containing compounds and can potentially serve as useful ligands of transition metal complexes.[5]

Results and Discussion

Treatment of 1-octynyldiphenylphosphine (**1a**) with dodecanethiol[6] (**2a**) in the presence of a catalytic amount of palladium acetate in ethanol for 1 h at 25 ˚C provided (*Z*)-1-diphenylphosphino-2-dodecylthio-1-octene (**3aa**) in 87% isolated yield and in 90% NMR yield (Table 1, entry 1).[7] Other palladium complexes such as $PdCl_2$ and $Pd_2(dba)_3$ also showed catalytic activity (entries 2 and 3). Nickel chloride and platinum chloride were inferior to palladium chloride (entries 4 and 5). Copper(II) chloride was ineffective (entry 6). The effect of solvent on the reaction was not significant (entries 7–11). The reactions proceeded in nonpolar solvents such as toluene and dichloromethane (entries 8 and 9) as well as in polar DMF (entry 10). It is worth noting that the reaction in water resulted in the highest yield of **3aa** (entry 11), although the reaction was heterogeneous.[8] To guarantee a wide scope of substrates, ethanol was selected as the best solvent.[9]

Table 1. Hydrothiolation of 1-Octynyldiphenylphosphine (**1a**) with Dodecanethiol (**2a**)[a]

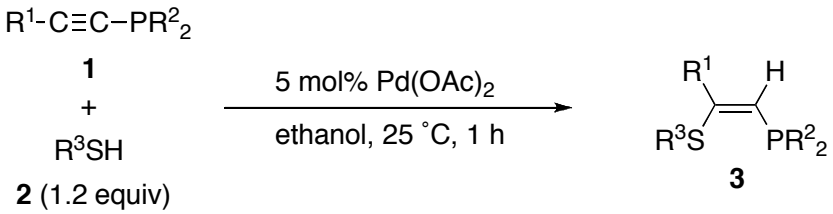


entry	catalyst	solvent	yield /%[b]
1	$Pd(OAc)_2$	ethanol	90 (87)
2	$PdCl_2$	ethanol	86
3	$Pd_2(dba)_3$[c]	ethanol	85
4	$PtCl_2$	ethanol	78
5	$NiCl_2$	ethanol	58
6	$CuCl_2$	ethanol	17
7	$Pd(OAc)_2$	THF	86
8	$Pd(OAc)_2$	1,2-dichloroethane	89
9	$Pd(OAc)_2$	toluene	89
10	$Pd(OAc)_2$	DMF	79
11	$Pd(OAc)_2$	water	92

[a] Conditions: **1a** (0.50 mmol), **2a** (0.60 mmol), solvent (3.0 mL), 25 ˚C, 1 h. [b] Based on ^{31}P NMR with a sufficient first decay period. An isolated yield is in parenthesis. [c] 2.5 mol% of $Pd_2(dba)_3$ was used.

A variety of 1-alkynylphosphines underwent the hydrothiolation reactions (Table 2). Sterically demanding 1-alkynylphopshines including **1b** and **1c** underwent the hydrothiolation smoothly (entries 1 and 2). Phenylethynylphosphine **1d** as well as terminal ethynylphosphine **1e** afforded the corresponding *anti*-adducts in good yields (entries 3 and 4). A variety of functional groups such as keto and hydroxy groups were compatible under the reaction conditions (entries 5–7). Pyridine-containing **3ia** (entry 8) can be useful for constructing supramolecular architectures. The addition of **2a** to bis(diphenylphosphino)ethyne (**1j**) took place to yield the corresponding *anti*-adduct **3ja** in 55% yield (entry 9). Alkynyldicyclohexylphosphine **1k** also underwent the hydrothiolation, although a longer reaction time was required to complete the reaction (entry 10).

Table 2. Palladium-Catalyzed Hydrothiolation of 1-Alkynylphosphines **1** with Thiols **2**[a]



entry	**1**	R^1	R^2	**2**	R^3	yield /%[b]
1	**1b**	*t*-Bu	Ph	**2a**	*n*-$C_{12}H_{25}$	93 (**3ba**)
2	**1c**	*i*-Pr	Ph	**2a**	*n*-$C_{12}H_{25}$	83 (**3ca**)
3	**1d**	Ph	Ph	**2a**	*n*-$C_{12}H_{25}$	81 (**3da**)
4	**1e**	H	Ph	**2a**	*n*-$C_{12}H_{25}$	78 (**3ea**)
5	**1f**	$EtO_2C(CH_2)_6$	Ph	**2a**	*n*-$C_{12}H_{25}$	77 (**3fa**)
6[c]	**1g**	4-Ac-C_6H_4	Ph	**2a**	*n*-$C_{12}H_{25}$	75 (**3ga**)
7	**1h**	PhCH(OH)	Ph	**2a**	*n*-$C_{12}H_{25}$	72 (**3ha**)
8	**1i**	3-pyridyl	Ph	**2a**	*n*-$C_{12}H_{25}$	78 (**3ia**)
9[d]	**1j**	Ph_2P	Ph	**2a**	*n*-$C_{12}H_{25}$	55 (**3ja**)
10[e]	**1k**	Ph	*c*-C_6H_{11}	**2a**	*n*-$C_{12}H_{25}$	82 (**3ka**)
11	**1a**	*n*-C_6H_{13}	Ph	**2b**	*t*-Bu	62 (**3ab**)
12	**1a**	*n*-C_6H_{13}	Ph	**2c**	Ph	82 (**3ac**)
13	**1a**	*n*-C_6H_{13}	Ph	**2d**	2-furfuryl	75 (**3ad**)
14	**1a**	*n*-C_6H_{13}	Ph	**2e**	cinnamyl	60 (**3ae**)
15	**1a**	*n*-C_6H_{13}	Ph	**2f**	4-Br-C_6H_4	80 (**3af**)
16	**1a**	*n*-C_6H_{13}	Ph	**2g**	$HO(CH_2)_3$	74 (**3ag**)
17	**1a**	*n*-C_6H_{13}	Ph	**2h**	*N*-acetylCys[f]	66 (**3ah**)
18[e]	**1k**	Ph	*c*-C_6H_{11}	**2i**	4-MeO-C_6H_4	70 (**3ki**)

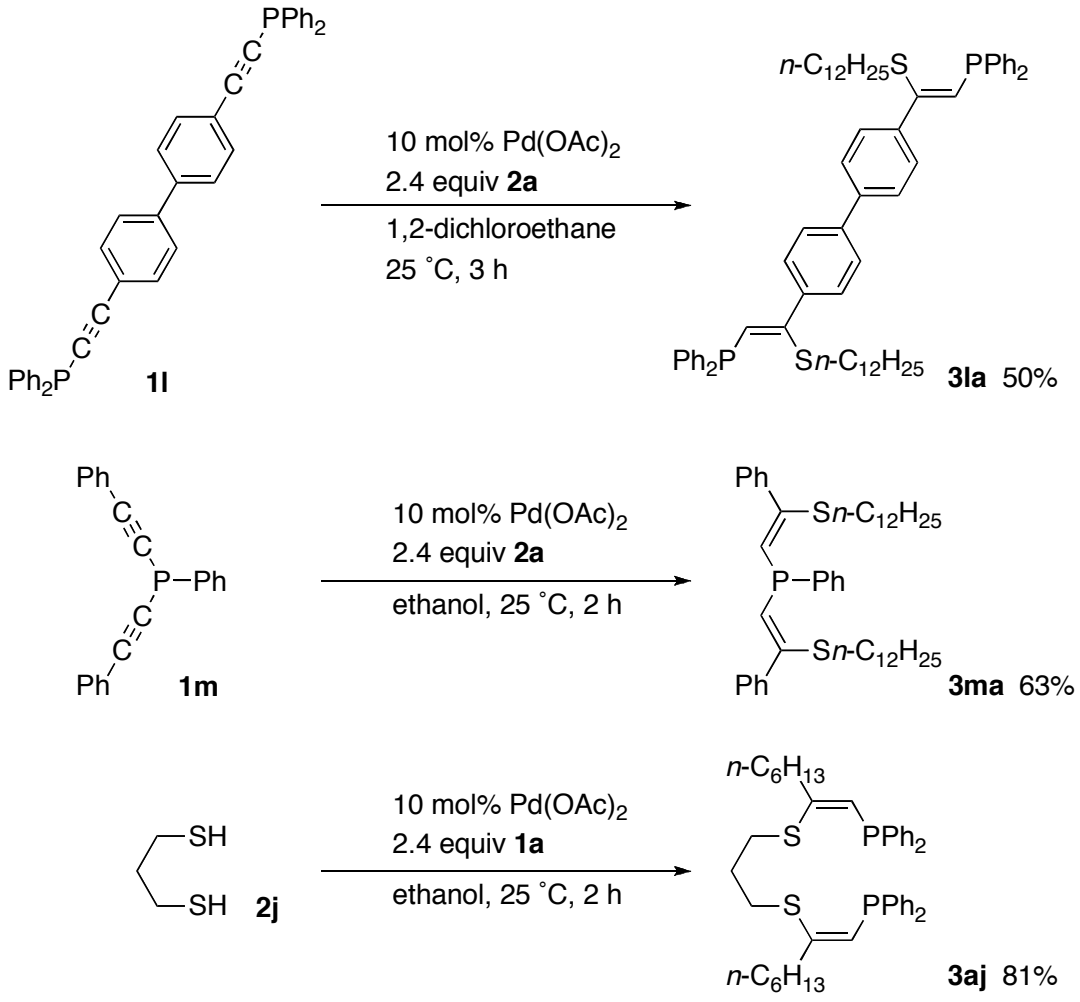
[a] Conditions: **1** (0.50 mmol), **2** (0.60 mmol), $Pd(OAc)_2$ (0.025 mmol), ethanol (3.0 mL), 25 ˚C, 1 h. [b] Isolated yields. [c] 1,2-Dichloroethane was used as a solvent. [d] The reaction was performed with 10 mol% of $Pd(OAc)_2$ in ethanol/1,2-dichloroethane (2 mL:1 mL) for 16 h. [e] The reaction was performed for 4 h. [f] *N*-Acetyl-L-cysteine was used.

The scope of thiol **2** was satisfactory (entries 11–18). Not only bulky thiol **2b** but also thiols having an additional functionality such as **2e–i** added to **1a** under the palladium catalysis. The successful hydrothiolation with protected cysteine **2h** implies that the reaction would be

applicable to modification of proteins and peptides (entry 17). The X-ray crystallographic analysis of **3ki** verified the *Z* stereochemistry of the products.

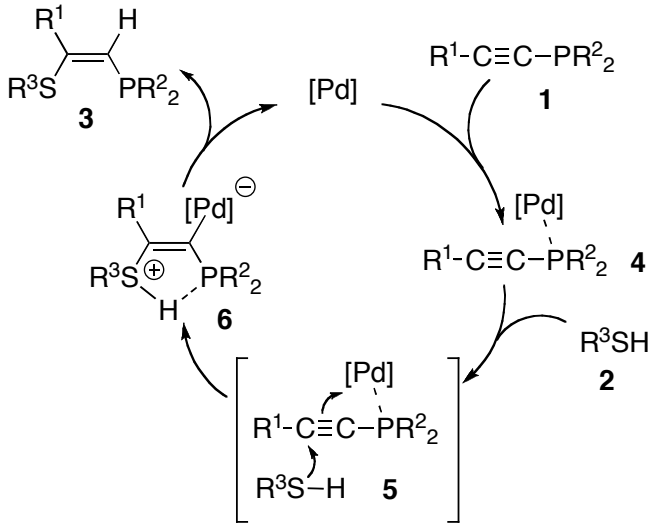
The reaction was efficient enough to allow for multiple hydrothiolation (Scheme 1). Treatment of biphenyl-based di(alkynylphosphine) **1l** with **2a** in the presence of a catalytic amount of $Pd(OAc)_2$ in 1,2-dichloroethane provided the corresponding bifunctional diphosphine **3la** in good yield. Di(phenylethynyl)phenylphosphine (**1m**) underwent hydrothiolation twice to yield **3ma**. However, attempted 3-fold hydrothiolation of tri(phenylethynyl)phosphine resulted in the formation of mixtures of the corresponding mono-, di- and triadducts. 1,3-Propanedithiol (**2j**) reacted with **1a** to afford an 81% yield of **3aj**. Such products having multicoordination sites can be useful building blocks for supramolecular architecture.

Scheme 1. Multiple Hydrothiolations



Reaction Mechanism. Judging from the regio- and stereoselectivity of the reaction, the author is tempted to assume the reaction mechanism as follows (Scheme 2). A palladium salt initially reacts with **1** to generate a palladium(1-alkynylphosphine) complex **4**. Thiol **2** attacks the carbon–carbon triple bond that is activated by the coordination to form intermediate **6**. Protonolysis of **6** affords **3** and regenerates the initial palladium species. The stereochemistry of the products suggests that the reaction should not proceed via oxidative addition of the thiol to a palladium complex followed by thiopalladation or hydropalladation[1,3] but via the coordination-assisted activation of the triple bond. The regioselectivity in the reaction of **1g** strongly supports his plausible mechanism that involves the transition state **5**. Without the coordination of the phosphorus center of **1g** to the palladium, the regioselectivity of the reaction of **1g** could be opposite because of the strong electron-withdrawing nature of the acetyl group. It is also worth noting that the corresponding phosphine oxide of **1a** completely resisted the reaction.

Scheme 2. Plausible Reaction Mechanism



Conclusion

The author has found a concise method for the synthesis of an array of (*Z*)-1-phosphino-2-thio-1-alkenes through the hydrothiolation of 1-alkynylphosphines. The method will create a new type of heteroatom-containing molecules which find applications in various fields of chemical science.

Experimental Procedure

Instrumentation and Chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in C_6D_6 or CD_3OD. Chemical shifts (δ) are in parts per million relative to benzene at 7.15 ppm for ^{1}H and relative to at 128.0 ppm for ^{13}C or methanol at 3.34 ppm for ^{1}H and at 49.0 ppm for ^{13}C. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in C_6D_6 or CD_3OD with 85% H_3PO_4 solution as an external standard. NMR yields were determined by fine ^{31}P NMR spectra with $(MeO)_3P=O$ as an internal standard. The first delay of ^{31}P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. For the preparation of **1**, chlorodiphenylphosphine was purchased from TCI. Chlorodicyclohexylphosphine was a gift from Hokko Chemical Industry Co., Ltd. Starting 1-alkynylphosphines **1** were prepared by the reactions of lithium acetylides with chlorophosphines or by nickel-catalyzed reactions of alkynes with chlorodiphenylphosphine described in Chapter 1. Palladium(II) acetate was obtained from TCI. All reactions were carried out under argon atmosphere.

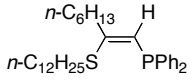
Typical Procedure for Palladium-Catalyzed *anti*-Hydrothiolation of 1-Alkynylphosphines

Palladium acetate (6 mg, 0.025 mmol) was placed in a 20-mL reaction flask under argon. A solution of **1a** (0.15 g, 0.50 mmol) in ethanol (3.0 mL) was added to the flask. Dodecanethiol (**2a**, 0.12 g, 0.60 mmol) was added, and the resulting solution was stirred for 1 h at 25 ˚C. The solvent was evaporated under reduced pressure, and the crude product obtained was

chromatographed on silica gel to afford **3aa** (0.22 g, 0.44 mmol, 87 %).

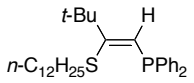
Characterization Data

(*Z*)-1-Diphenylphosphino-2-dodecylthio-1-octene (3aa)



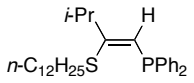
IR (neat) 3053, 2927, 2854, 2342, 1585, 1555, 1480, 1456, 1433, 1378, 1094, 1027, 739, 695 cm^{-1}; ^1H NMR (C_6D_6) δ 0.88 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H), 1.10–1.36 (m, 24H), 1.45 (tt, *J* = 7.0, 7.5 Hz, 2H), 1.57 (tt, *J* = 7.0, 7.5 Hz, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 6.33 (s, 1H), 7.01–7.07 (m, 2H), 7.08–7.14 (m, 4H), 7.50–7.57 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.29, 14.38, 23.03, 23.10, 29.03, 29.08, 29.34 (d, *J* = 1.4 Hz), 29.59, 29.81, 29.92, 30.05, 30.10 (2C), 30.19, 31.70 (d, *J* = 6.3 Hz), 31.97, 32.32, 38.24 (d, *J* = 4.3 Hz), 128.33, 128.35 (d, *J* = 14.9 Hz), 128.68 (d, *J* = 6.6 Hz), 133.14 (d, *J* = 19.0 Hz), 140.63 (d, *J* = 12.4 Hz), 153.60 (d, *J* = 24.8 Hz); ^{31}P NMR (C_6D_6) δ –25.65. Found: C, 77.13; H, 10.10%. Calcd for $C_{32}H_{49}PS$: C, 77.37; H, 9.94%.

(*Z*)-3,3-Dimethyl-1-diphenylphosphino-2-dodecylthio-1-butene (3ba)



IR (neat) 3053, 2924, 2854, 1585, 1555, 1464, 1433, 1356, 1231, 1096, 951, 835, 739, 695 cm^{-1}; ^1H NMR (C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 3H), 1.19 (s, 9H), 1.16–1.36 (m, 18H), 1.60 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.98 (dd, *J* = 1.5, 7.5 Hz, 2H), 6.75 (s, 1H), 7.02–7.07 (m, 2H), 7.08–7.13 (m, 4H), 7.51–7.57 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.33, 23.08, 29.29, 29.64 (2C), 29.77, 29.92, 30.01, 30.06, 30.07, 30.12, 32.30, 38.70 (d, *J* = 12.0 Hz), 41.30 (d, *J* = 3.8 Hz), 128.47, 128.74 (d, *J* = 6.3 Hz), 133.10 (d, *J* = 10.0 Hz), 133.28 (d, *J* = 6.8 Hz), 140.82 (d, *J* = 12.9 Hz), 163.66 (d, *J* = 22.5 Hz); ^{31}P NMR (C_6D_6) δ –24.06. Found: C, 76.65; H, 9.76%. Calcd for $C_{30}H_{45}PS$: C, 76.87; H, 9.68%.

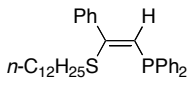
(*Z*)-3-Methyl-1-diphenylphosphino-2-dodecylthio-1-butene (3ca)



IR (neat) 3053, 2959, 2925, 2854, 2364, 1540, 1479, 1458, 1433, 1380, 1094, 740, 695 cm^{-1}; ^1H NMR (C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 7.0 Hz,

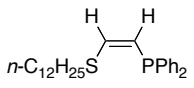
6H), 1.12–1.35 (m, 18H), 1.45 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.50 (sept, *J* = 7.0 Hz, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 6.43 (s, 1H), 7.01–7.07 (m, 2H), 7.08–7.14 (m, 4H), 7.50–7.57 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.33, 22.55, 23.08, 29.05, 29.58, 29.78, 29.90, 30.02, 30.07, 30.08, 30.13, 32.30, 32.86 (d, *J* = 7.1 Hz), 35.27 (d, *J* = 4.4 Hz), 127.27 (d, *J* = 8.1 Hz), 128.34, 128.71 (d, *J* = 6.6 Hz), 133.09 (d, *J* = 19.6 Hz), 140.78 (d, *J* = 12.9 Hz), 159.70 (d, *J* = 23.9 Hz); ^{31}P NMR (C_6D_6) δ –25.61. Found: C, 76.64; H, 9.66%. Calcd for $C_{29}H_{43}PS$: C, 76.60; H, 9.53%.

(*Z*)-2-Diphenylphosphino-1-dodecylthio-1-phenylethene (3da)



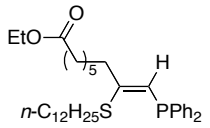
IR (neat) 3053, 2924, 2854, 2333, 1585, 1540, 1480, 1433, 1305, 1232, 1094, 1027, 740, 695 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 3H), 0.95–1.36 (m, 20H), 2.33 (t, *J* = 7.5 Hz, 2H), 6.73 (s, 1H), 7.01–7.13 (m, 9H), 7.49–7.57 (m, 6H); ^{13}C NMR (C_6D_6) δ 14.38, 23.10, 28.68, 29.43, 29.80, 29.83, 29.97, 29.99, 30.08 (2C), 32.31, 33.14 (d, *J* = 4.4 Hz), 128.40 (d, *J* = 2.0 Hz), 128.49, 128.60, 128.71, 128.78 (d, *J* = 6.8 Hz), 133.01 (d, *J* = 10.5 Hz), 133.31 (d, *J* = 19.6 Hz), 140.26 (d, *J* = 4.8 Hz), 140.41 (d, *J* = 12.0 Hz), 152.42 (d, *J* = 25.8 Hz); ^{31}P NMR (C_6D_6) δ –23.27. Found: C, 78.37; H, 8.46%. Calcd for $C_{32}H_{41}PS$: C, 78.64; H, 8.46%.

(*Z*)-2-Diphenylphosphino-1-dodecylthioethene (3ea)



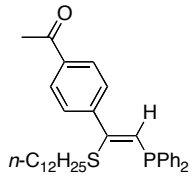
IR (neat) 3053, 2925, 2853, 1586, 1532, 1467, 1433, 1269, 1097, 1027, 820, 740, 695 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.92 (t, *J* = 7.0 Hz, 3H), 1.06–1.42 (m, 20H), 2.33 (t, *J* = 7.5 Hz, 2H), 6.22 (d, *J* = 10.5 Hz, 1H), 6.72 (dd, *J* = 10.5, 15.5 Hz, 1H), 7.01–7.05 (m, 2H), 7.06–7.11 (m, 4H), 7.48–7.54 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.36, 23.10, 28.76, 29.50, 29.80, 29.87, 30.01, 30.08 (2C), 30.70, 32.31, 34.74 (d, *J* = 4.8 Hz), 124.38 (d, *J* = 11.0 Hz), 128.50, 128.73 (d, *J* = 6.6 Hz), 133.11 (d, *J* = 19.1 Hz), 139.37 (d, *J* = 10.5 Hz), 144.17 (d, *J* = 27.1 Hz); ^{31}P NMR (C_6D_6) δ –25.73. Found: C, 75.90; H, 9.33%. Calcd for $C_{26}H_{37}PS$: C, 75.68; H, 9.04%.

Ethyl (*Z*)-9-diphenylphosphino-8-dodecylthio-8-nonenoate (3fa)



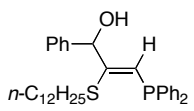
IR (neat) 2926, 2854, 2332, 1737, 1467, 1434, 1374, 1181, 1096, 1027, 740, 696 cm^{-1}; ^1H NMR (C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H), 1.10–1.36 (m, 22H), 1.40–1.60 (m, 6H), 2.12 (t, *J* = 7.5 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.52 (t, *J* = 7.5 Hz, 2H), 3.97 (q, *J* = 7.5 Hz, 2H), 6.32 (s, 1H), 7.02–7.08 (m, 2H), 7.09–7.16 (m, 4H), 7.50–7.56 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.33, 14.36, 23.09, 25.23, 28.96, 29.03, 29.11 (d, *J* = 1.9 Hz), 29.16, 29.59, 29.79, 29.92, 30.04, 30.08, 30.09, 30.19, 31.71 (d, *J* = 6.1 Hz), 32.31, 34.27, 38.09 (d, *J* = 3.8 Hz), 59.96, 128,35, 128.52 (d, *J* = 8.6 Hz), 128.70 (d, *J* = 6.8 Hz), 133.13 (d, *J* = 19.1 Hz), 140.61 (d, *J* = 11.9 Hz), 153.43 (d, *J* = 24.9 Hz), 172.85; ^{31}P NMR (C_6D_6) δ –25.68. Found: C, 73.72; H, 9.44%. Calcd for $C_{35}H_{53}O_2PS$: C, 73.90; H, 9.39%.

(*Z*)-1-(4-Acetylphenyl)-2-diphenylphosphino-1-dodecylthioethene (3ga)



IR (neat) 3053, 2925, 2854, 1684, 1600, 1433, 1402, 1356, 1265, 1178, 956, 853, 742, 695 cm^{-1}; ^1H NMR (C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 3H), 1.01–1.36 (m, 20H), 2.10 (s, 3H), 2.92 (t, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 1.5 Hz, 1H), 7.03–7.09 (m, 2H), 7.10–7.15 (m, 4H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.50–7.57 (m, 4H), 7.74 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (C_6D_6) δ 14.35, 23.08, 26.16, 28.70 (d, *J* = 1.0 Hz), 29.42, 29.78, 29.82, 29.94, 29.99, 30.06 (2C), 32.29, 33.17 (d, *J* = 4.3 Hz), 128.36 (d, *J* = 2.4 Hz), 128.70, 128.81, 128.87 (d, *J* = 6.6 Hz), 133.33 (d, *J* = 20.0 Hz), 135.30 (d, *J* = 11.4 Hz), 137.28, 139.95 (d, *J* = 11.5 Hz), 144.12 (d, *J* = 4.8 Hz), 150.99 (d, *J* = 26.3 Hz), 195.80; ^{31}P NMR (C_6D_6) δ –22.25. Found: C, 77.20; H, 8.42%. Calcd for $C_{34}H_{43}OPS$: C, 76.94; H, 8.17%.

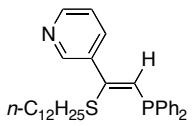
(*Z*)-3-Diphenylphosphino-2-dodecylthio-1-phenyl-2-propen-1-ol (3ha)



IR (neat) 3388, 3055, 2925, 2854, 2333, 1585, 1454, 1435, 1378, 1187, 1068, 865, 741, 697 cm^{-1}; ^1H NMR (C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 3H), 1.00–1.37 (m, 20H), 2.16 (d, *J* = 4.5 Hz, 1H), 2,43–2.57 (m, 2H), 5.23 (d, *J* = 4.5 Hz, 1H),

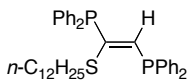
7.00–7.16 (m, 10H), 7.40 (d, J = 7.5 Hz, 2H), 7.46–7.55 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.36, 23.09, 28.97, 29.49, 29.79, 29.87, 29.96, 30.01, 30.08 (2C), 32.30, 33.75 (d, J = 6.8 Hz), 77.55 (d, J = 4.3 Hz), 127.17, 128.52 (2C), 128.54, 128.55, 128.75 (d, J = 6.6 Hz), 128.76 (d, J = 6.6 Hz), 132.71 (d, J = 10.0 Hz), 133.21 (d, J = 19.6 Hz), 133.24 (d, J = 19.0 Hz), 139.92 (d, J = 11.9 Hz), 140.19 (d, J = 11.5 Hz), 142.36 (d, J = 1.5 Hz), 153.65 (d, J = 24.4 Hz); ^{31}P NMR (C_6D_6) δ –25.54. Found: C, 76.29; H, 8.50%. Calcd for $C_{33}H_{43}OPS$: C, 76.41; H, 8.35%.

(*Z*)-2-Diphenylphosphino-1-dodecylthio-1-(3-pyridyl)ethene (3ia)



IR (neat) 2925, 2854, 1566, 1459, 1433, 1410, 1184, 1095, 1025, 740, 695 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.91 (t, J = 7.0 Hz, 3H), 0.96–1.36 (m, 20H), 2.19 (t, J = 7.5 Hz, 2H), 6.67 (s, 1H), 6.67 (dd, J = 5.0, 8.5 Hz, 1H), 7.03–7.13 (m, 6H), 7.46 (ddd, J = 1.5, 2.5, 8.5 Hz, 1H), 7.47–7.52 (m, 4H), 8.45 (dd, J = 1.5, 5.0 Hz, 1H), 9.00 (d, J = 2.5 Hz, 1H); ^{13}C NMR (C_6D_6) δ 14.36, 23.09, 28.59, 29.37, 29.79 (2C), 29.82, 29.97, 30.06 (2C), 32.30, 33.05 (d, J = 3.9 Hz), 123.13, 128.64, 128.84 (d, J = 6.8 Hz), 133.28 (d, J = 19.5 Hz), 134.87 (d, J = 2.4 Hz), 135.14 (d, J = 11.5 Hz), 135.51 (d, J = 4.8 Hz), 139.88 (d, J = 11.4 Hz), 148.72 (d, J = 26.6 Hz), 149.63 (d, J = 2.0 Hz), 149.90; ^{31}P NMR (C_6D_6) δ –22.64. Found: C, 76.02; H, 8.36%. Calcd for $C_{31}H_{40}NPS$: C, 76.03; H, 8.23%.

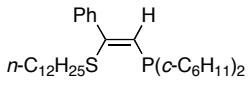
(*Z*)-1,2-Bis(diphenylphosphino)-1-dodecylthioethene (3ja)



IR (neat) 3070, 2924, 2853, 2364, 1719, 1654, 1434, 1307, 1237, 1152, 1091 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.91 (t, J = 7.0 Hz, 3H), 1.07–1.35 (m, 18H), 1.56 (tt, J = 7.0, 7.5 Hz, 2H), 3.00 (dt, J = 1.0, 7.5 Hz, 2H), 6.67 (dd, J = 2.0, 4.5 Hz, 1H), 6.97–7.08 (m, 12H), 7.41–7.53 (m, 8H); ^{13}C NMR (C_6D_6) δ 14.33, 23.08, 28.93, 29.50, 29.79, 29.86, 30.00, 30.07, 30.08, 30.39 (d, J = 2.4 Hz), 32.30, 33.86 (dd, J = 5.8, 18.1 Hz), 128.45, 128.67 (d, J = 6.3 Hz), 128.89 (d, J = 7.1 Hz), 129.34, 133.15 (d, J = 19.1 Hz), 134.45 (d, J = 20.1 Hz), 136.07 (d, J = 12.9 Hz), 140.17 (dd, J = 1.5, 12.5 Hz), 140.83 (dd, J = 3.8, 16.3 Hz), 152.11 (dd, J = 20.5, 41.0 Hz); ^{31}P NMR (C_6D_6) δ –22.93, –4.30. Found: C, 76.68; H, 7.74%. Calcd for

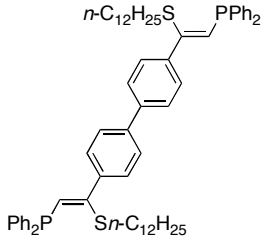
$C_{38}H_{46}P_2S$: C, 76.48; H, 7.77%.

(*Z*)-2-Dicyclohexylphosphino-1-dodecylthio-1-phenylethene (3ka)



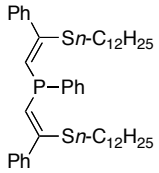
IR (neat) 2926, 2853, 1538, 1486, 1447, 1178, 1073, 1029, 1000, 907, 850, 752, 697 cm^{-1}; ^1H NMR (C_6D_6) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.01–1.42 (m, 30H), 1.54–2.00 (m, 12H), 2.37 (t, *J* = 7.5 Hz, 2H), 6.36 (d, *J* = 4.0 Hz, 1H), 7.04–7.17 (m, 3H), 7.62 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (C_6D_6) δ 14.37, 23.10, 26.91, 27.56 (d, *J* = 4.8 Hz), 27.65, 28.70 (d, *J* = 1.0 Hz), 29.58, 29.80, 29.86 (d, *J* = 8.1 Hz), 29.93, 30.04, 30.06, 30.09, 30.10, 31.08 (d, *J* = 16.8 Hz), 32.32, 33.07 (d, *J* = 3.9 Hz), 35.26 (d, *J* = 12.4 Hz), 128.35, 128.43, 128.63, 128.89 (d, *J* = 19.5 Hz), 141.61 (d, *J* = 5.3 Hz), 154.16 (d, *J* = 25.3 Hz); ^{31}P NMR (C_6D_6) δ –19.44. Found: C, 76.86; H, 10.58%. Calcd for $C_{32}H_{53}PS$: C, 76.75; H, 10.67%.

4,4'-Bis{(*Z*)-2-diphenylphosphino-1-dodecylthio-1-ethenyl}biphenyl (3la)



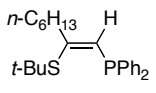
IR (nujol) 2923, 2854, 1685, 1583, 1457, 1377, 1304, 1268, 1092, 1026, 915, 815, 744, 698 cm^{-1}; ^1H NMR (C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 6H), 1.03–1.34 (m, 36H), 1.38 (tt, *J* = 7.0, 7.5 Hz, 4H), 2.42 (t, *J* = 7.0 Hz, 4H), 6.86 (d, *J* = 1.5 Hz, 2H), 7.04–7.09 (m, 4H), 7.10–7.07 (m, 8H), 7.46 (d, *J* = 8.5 Hz, 4H), 7.56–7.62 (m, 8H), 7.63 (d, *J* = 8.5 Hz, 4H); ^{13}C NMR (C_6D_6) δ 14.36, 23.09, 28.72 (d, *J* = 1.0 Hz), 29.47, 29.79, 29.85, 30.01 (2C), 30.07 (2C), 32.29, 33.30 (d, *J* = 3.4 Hz), 127.38, 128.58, 128.84 (d, *J* = 6.8 Hz), 128.98 (d, *J* = 1.9 Hz), 133.34 (d, *J* = 19.5 Hz), 133.51 (d, *J* = 10.5 Hz), 139.44 (d, *J* = 4.8 Hz), 140.38 (d, *J* = 11.9 Hz), 140.87, 151.83 (d, *J* = 26.3 Hz); ^{31}P NMR (C_6D_6) δ –22.85. Found: C, 78.57; H, 8.19%. Calcd for $C_{64}H_{80}P_2S_2$: C, 78.81; H, 8.27%. m.p.: 77.0–79.0 ˚C.

Di{(*Z*)-2-Dodecylthio-2-phenylethenyl}phenylphosphine (3ma)



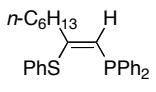
IR (neat) 3054, 2924, 2854, 1486, 1466, 1434, 1074, 1028, 909, 741, 697 cm^{-1}; ^1H NMR (C_6D_6) δ 0.91 (t, *J* = 7.0 Hz, 6H), 1.06–1.37 (m, 36H), 1.40–1.50 (m, 4H), 2.34–2.47 (m, 4H), 6.70 (d, *J* = 1.0 Hz, 2H), 7.04–7.21 (m, 9H), 7.60–7.65 (m, 4H), 7.70–7.77 (m, 2H); ^{13}C NMR (C_6D_6) δ 14.36, 23.10, 28.88 (d, *J* = 1.0 Hz), 29.55, 29.82, 29.91, 30.08, 30.12 (2C), 30.20, 32.32, 33.19 (d, *J* = 4.3 Hz), 128.39, 128.41 (2C), 128.65, 128.80 (d, *J* = 6.3 Hz), 132.93 (d, *J* = 19.6 Hz), 135.11 (d, *J* = 9.5 Hz), 140.52 (d, *J* = 4.8 Hz), 141.26 (d, *J* = 12.9 Hz), 150.41 (d, *J* = 26.8 Hz); ^{31}P NMR (C_6D_6) δ –39.13. Found: C, 77.54; H, 9.49%. Calcd for $C_{46}H_{67}PS_2$: C, 77.26; H, 9.44%.

(*Z*)-2-(1,1-Dimethylethylthio)-1-diphenylphosphino-1-octene (3ab)



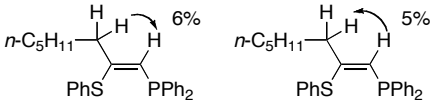
IR (neat) 3053, 2927, 2855, 1585, 1458, 1433, 1364, 1158, 1095, 1027, 740, 695 cm^{-1}; ^1H NMR (C_6D_6) δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.16–1.30 (m, 6H), 1.31 (s, 9H), 1.65 (tt, *J* = 7.0, 7.5 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 6.62 (s, 1H), 7.01–7.06 (m, 2H), 7.07–7.13 (m, 4H), 7.48–7.54 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.27, 23.01, 29.08, 29.52 (d, *J* = 2.4 Hz), 31.96, 32.23 (d, *J* = 1.5 Hz), 42.32 (d, *J* = 2.4 Hz), 46.97 (d, *J* = 1.9 Hz), 128.27, 128.65 (d, *J* = 6.3 Hz), 133.19 (d, *J* = 19.1 Hz), 138.14 (d, *J* = 7.6 Hz), 140.78 (d, *J* = 13.4 Hz), 152.84 (d, *J* = 24.8 Hz); ^{31}P NMR (C_6D_6) δ –24.02. Found: C, 75.02; H, 8.36%. Calcd for $C_{24}H_{33}PS$: C, 74.96; H, 8.65%.

(*Z*)-1-Diphenylphosphino-2-phenylthio-1-octene (3ac)

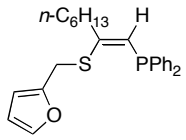


IR (neat) 3054, 2927, 2855, 2340, 1583, 1478, 1436, 1378, 1094, 1968, 1025, 999, 740, 695 cm^{-1}; ^1H NMR (C_6D_6) δ 0.81 (t, *J* = 7.0 Hz, 3H), 1.05–1.20 (m, 6H), 1.47 (tt, *J* = 7.0, 7.5 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 6.54 (s, 1H), 6.86–6.95 (m, 3H), 7.04–7.09 (m, 2H), 7.10–7.17 (m, 4H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.54–7.60 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.21, 22.86, 28.78, 29.25 (d, *J* = 2.0 Hz), 31.77, 38.37 (d, *J* = 3.8 Hz), 127.40, 128.51, 128.80 (d, *J* = 6.8 Hz), 129.10, 131.50 (d, *J* = 10.0 Hz), 132.43, 133.21 (d, *J* = 19.1 Hz), 134.28 (d, *J* = 5.3

Hz), 140.35 (d, J = 12.0 Hz), 153.06 (d, J = 25.4 Hz); ^{31}P NMR (C_6D_6) δ –23.88. Found: C, 76.93; H, 7.18%. Calcd for $C_{26}H_{29}PS$: C, 77.19; H, 7.23%.

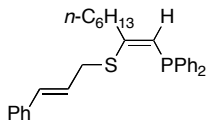
NOE analysis: 

(*Z*)-2-(2-Furylmethylthio)-1-diphenylphosphino-1-octene (3ad)



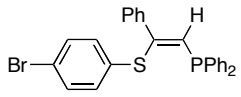
IR (neat) 2928, 2855, 1557, 1436, 1242, 1151, 1069, 1010, 934, 885, 805, 739, 695 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.86 (t, J = 7.0 Hz, 3H), 1.10–1.27 (m, 6H), 1.47 (tt, J = 7.0, 7.5 Hz, 2H), 2.27 (t, J = 7.5 Hz, 2H), 3.65 (s, 2H), 5.99 (dd, J = 2.0, 3.5 Hz, 1H), 6.05 (dd, J = 1.0, 3.5 Hz, 1H), 6.32 (s, 1H), 7.00 (dd, J = 1.0, 2.0 Hz, 1H), 7.02–7.06 (m, 2H), 7.07–7.12 (m, 4H), 7.45–7.51 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.24, 22.96, 28.56 (d, J = 6.3 Hz), 28.96, 29.03 (d, J = 1.4 Hz), 31.88, 38.28 (d, J = 3.8 Hz), 107.86 (d, J = 0.9 Hz), 110.77, 128.38, 128.70 (d, J = 6.6 Hz), 129.60 (d, J = 9.0 Hz), 133.10 (d, J = 19.1 Hz), 140.33 (d, J = 12.0 Hz), 142.00, 151.96, 152.78 (d, J = 24.3 Hz); ^{31}P NMR (C_6D_6) δ –25.72. Found: C, 73.68; H, 7.13%. Calcd for $C_{25}H_{29}OPS$: C, 73.50; H, 7.15%.

(*Z*)-1-Diphenylphosphino-2-{(*E*)-3-phenyl-2-propenylthio}-1-octene (3ae)



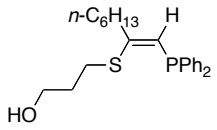
IR (neat) 3026, 2929, 2855, 2334, 1554, 1436, 1217, 1095, 1027, 962, 740, 695 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.87 (t, J = 7.0 Hz, 3H), 1.10–1.28 (m, 6H), 1.55 (tt, J = 7.0, 7.5 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 3.24 (dd, J = 1.5, 7.5 Hz, 2H), 6.06 (dt, J = 7.5, 15.5 Hz, 1H), 6.30 (d, J = 15.5 Hz, 1H), 6.36 (s, 1H), 7.00–7.20 (m, 11H), 7.48–7.56 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.23, 22.98, 29.06, 29.13 (d, J = 1.9 Hz), 31.93, 34.77 (d, J = 6.3 Hz), 38.60 (d, J = 4.3 Hz), 126,05, 126.73, 127.67, 128.37, 128.70 (d, J = 5.6 Hz), 128.73, 129.91 (d, J = 8.6 Hz), 132.55, 133.13 (d, J = 19.1 Hz), 137.21, 140.41 (d, J = 12.0 Hz), 152.97 (d, J = 24.8 Hz); ^{31}P NMR (C_6D_6) δ –25.54. Found: C, 78.57; H, 7.70%. Calcd for $C_{29}H_{33}PS$: C, 78.34; H, 7.48%.

(*Z*)-2-(4-Bromophenylthio)-1-diphenylphosphino-1-octene (3af)



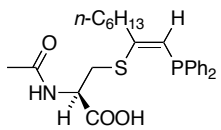
IR (neat) 2926, 2855, 1568, 1471, 1435, 1379, 1089, 1068, 1010, 815, 740, 696 cm^{-1}; ^1H NMR (C_6D_6) δ 0.82 (t, *J* = 7.5 Hz, 3H), 1.02–1.22 (m, 6H), 1.42 (tt, *J* = 7.0, 7.5 Hz, 2H), 2.14 (t, *J* = 7.5 Hz, 2H), 6.53 (s, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 7.03–7.09 (m, 2H), 7.10–7.15 (m, 4H), 7.50–7.56 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.25, 22.87, 28.72, 29.12 (d, *J* = 2.0 Hz), 31.77, 38.32 (d, *J* = 3.4 Hz), 121.62, 128.63, 128.84 (d, *J* = 6.8 Hz), 132.19, 132.62 (d, *J* = 10.9 Hz), 133.17 (d, *J* = 19.1 Hz), 133.41 (d, *J* = 5.8 Hz), 133.57, 140.03 (d, *J* = 11.5 Hz), 152.02 (d, *J* = 24.8 Hz); ^{31}P NMR (C_6D_6) δ –23.67. Found: C, 64.39; H, 5.78%. Calcd for $C_{26}H_{28}PSBr$: C, 64.60; H, 5.84%.

(*Z*)-1-Diphenylphosphino-2-(3-hydroxypropylthio)-1-octene (3ag)



IR (neat) 3336, 3053, 2928, 2855, 1555, 1433, 1027, 740, 696 cm^{-1}; ^1H NMR (C_6D_6) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.15–1.30 (m, 6H), 1.48–1.63 (m, 4H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 3.43 (t, *J* = 6.0 Hz, 2H), 6.32 (s, 1H), 7.01–7.07 (m, 2H), 7.08–7.14 (m, 4H), 7.49–7.56 (m, 4H); ^{13}C NMR (C_6D_6) δ 14.28, 23.00, 28.17 (d, *J* = 5.8 Hz), 29.01, 29.24 (d, *J* = 1.9 Hz), 31.93, 32.66, 38.01 (d, *J* = 4.3 Hz), 60.79, 128.42, 128.61 (d, *J* = 8.1 Hz), 128.72 (d, *J* = 6.1 Hz), 133.11 (d, *J* = 19.1 Hz), 140.32 (d, *J* = 11.0 Hz), 153.43 (d, *J* = 24.8 Hz); ^{31}P NMR (C_6D_6) δ –25.54. Found: C, 71.67; H, 8.19%. Calcd for $C_{23}H_{31}OPS$: C, 71.47; H, 8.08%.

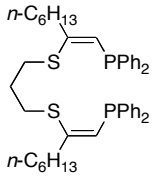
(*S*)-*N*-Acetyl-{(*Z*)-2-diphenylphosphino-1-hexylethenylthio}-L-cysteine (3ah)



IR (nujol) 3349, 2924, 2854, 2483, 2194, 1740, 1700, 1653, 1456, 1377, 1308, 1226, 1027, 817, 739, 694 cm^{-1}; ^1H NMR (CD_3OD) δ 0.77 (t, *J* = 7.0 Hz, 3H), 1.13–1.28 (m, 6H), 1.48 (tt, *J* = 7.0, 7.5 Hz, 2H), 1.88 (s, 3H), 2.40 (t, *J* = 7.5 Hz, 2H), 2.88–2.96 (m, 1H), 3.14–3.22 (m, 1H), 4.36–4.46 (m, 1H), 6.15 (s, 1H), 7.10–7.22 (m, 10H); ^{13}C NMR (CD_3OD) δ 14.37, 22.67, 23.60, 29.48, 29.79, 32.61, 33.57, 38.52, 53.94, 129.40, 131.15, 133.51 (d, *J* = 21.0 Hz), 133.68 (d, *J* = 21.9 Hz), 140.55 (d, *J* = 41.5 Hz), 153.15

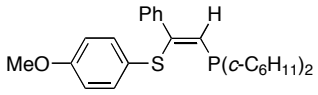
(d, J = 23.4 Hz), 173.11, 173.70; ^{31}P NMR (CD_3OD) δ –22.46. Found: C, 65.44; H, 6.85%. Calcd for $C_{25}H_{32}NO_3PS$: C, 65.62; H, 7.05%. m.p.: 49.0–51.0 °C. $[\alpha]_D^{25}$ = +100 (*c* 0.32, methanol).

1,3-Bis{(*Z*)-2-diphenylphosphino-1-hexylethenylthio}propane (3aj)



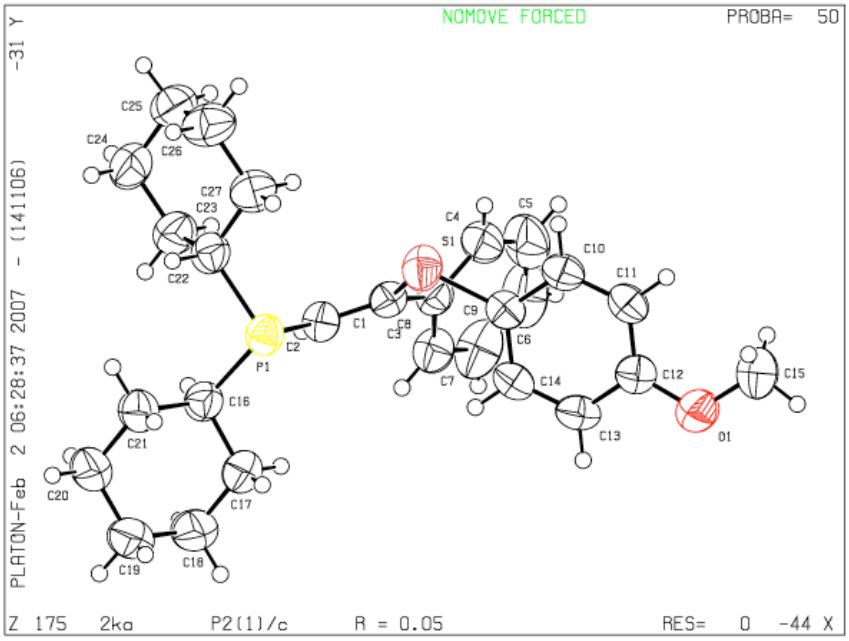
IR (neat) 3052, 2927, 2855, 1585, 1554, 1480, 1436, 1240, 1095, 1026, 798, 740, 695 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.88 (t, J = 7.0 Hz, 6H), 1.15–1.32 (m, 12H), 1.50–1.63 (m, 6H), 2.32 (t, J = 7.5 Hz, 4H), 2.64 (t, J = 7.0 Hz, 4H), 6.32 (s, 2H), 7.02–7.07 (m, 4H), 7.08–7.14 (m, 8H), 7.48–7.54 (m, 8H); ^{13}C NMR (C_6D_6) δ 14.30, 23.02, 29.03, 29.32 (d, J = 1.4 Hz), 29.95, 29.98, 31.97, 38.08 (d, J = 4.3 Hz), 128.37, 128.71 (d, J = 6.6 Hz), 129.28 (d, J = 8.6 Hz), 133.10 (d, J = 19.1 Hz), 140.47 (d, J = 12.0 Hz), 153.10 (d, J = 24.8 Hz); ^{31}P NMR (C_6D_6) δ –25.36. Found: C, 73.93; H, 7.99%. Calcd for $C_{43}H_{54}P_2S_2$: C, 74.10; H, 7.81%.

(*Z*)-2-Dicyclohexylphosphino-1-(4-methoxyphenylthio)-1-phenylethene (3ki)



IR (nujol) 2920, 2853, 1592, 1573, 1495, 1436, 1291, 1247, 1185, 1035, 830, 754, 696 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.12–1.50 (m, 10H), 1.56–2.05 (m, 12H), 3.00 (s, 3H), 6.42 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 4.5 Hz, 1H), 6.90 (dd, J = 7.5, 7.5 Hz, 1H), 7.00 (dd, J = 7.5, 7.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H); ^{13}C NMR (C_6D_6) δ 26.89, 27.56 (d, J = 4.3 Hz), 27.64, 29.96 (d, J = 8.5 Hz), 31.12 (d, J = 16.8 Hz), 35.35 (d, J = 12.9 Hz), 54.46, 114.60, 126.08 (d, J = 3.8 Hz), 128.19, 128.26, 128.63, 133.12, 133.86 (d, J = 20.1 Hz), 141.24 (d, J = 4.9 Hz), 153.60 (d, J = 24.9 Hz), 159.04; ^{31}P NMR (C_6D_6) δ –17.39. m.p.: 144.0–146.0 °C. CCDC No.: 635602.

Figure 1. ORTEP diagram of **3ki**



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(3) (a) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902–5903. (b) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108–5114.

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(7) The perfect *Z* stereoselectivity was observed at the initial stage of the reaction.

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(9) No reactions took place in the absence of the catalyst in ethanol or in water.

Chapter 3

Regio- and Stereoselective Hydroamidation of 1-Alkynylphosphine Sulfides Catalyzed by Cesium Base

Regio- and stereoselective hydroamidation of 1-alkynylphosphine sulfides proceeds in the presence of cesium carbonate to provide (*E*)-2-amino-1-thiophosphinyl-1-alkenes. Asymmetric hydrogenation of the adducts catalyzed by an iridium complex followed by desulfidation yields 2-amino-1-phosphinoalkanes, which offers a new approach to chiral N,P-ligands that will potentially serve as ligands in asymmetric reactions.

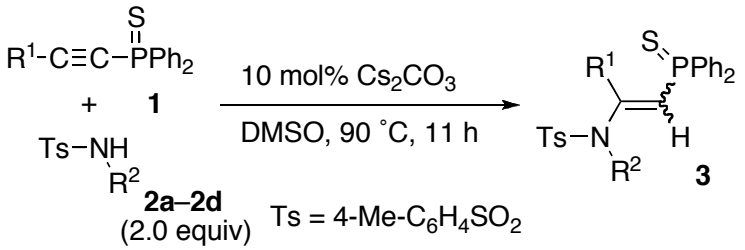
Introduction

Organophosphines play invaluable roles in organic synthesis, especially as ligands for transition metal catalysts. Development of novel approaches to organophosphines is thus quite important. The author has been focusing on 1-alkynylphosphine derivatives as precursors of new phosphines and developed addition reactions of diphenylphosphine (Chapter 1) and thiols (Chapter 2). Considering the importance of bidentate aminophosphine ligands in homogeneous transition metal catalysis,[1] he investigated the addition reaction of nitrogen nucleophiles. In this chapter, the author describes cesium-catalyzed addition of amides or imides to 1-alkynylphosphine sulfides,[2–4] directed toward the construction of vicinal N,P-frameworks.

Results and Discussion

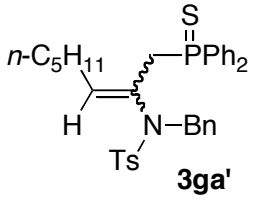
Treatment of diphenyl(phenylethynyl)phosphine sulfide (**1a**) with 2 equivalents of *N*-benzyltosylamide (**2a**) in the presence of a catalytic amount of cesium carbonate (10 mol%) in DMSO for 11 h at 90 ˚C provided 1-(*N*-benzyl-*N*-tosylamino)-2-diphenylthiophosphinyl-1-phenylethene (**3aa**) in 84% isolated yield with an *E*/*Z* ratio of 96/4 (Table 1, entry 1). Recrystallization of the product allowed for the isolation of the *E* isomer in 71% yield.[5] Aprotic polar solvents, such as DMSO, DMF, and NMP, are the solvents of choice. The reactions in 1,4-dioxane (bp 100 ˚C), acetonitrile (bp 82 ˚C), and toluene (bp 111 ˚C) at reflux afforded the product in moderate yields. In protic solvents such as 2-propanol at reflux, a trace amount of the product was obtained. Cesium carbonate is the most effective base. The uses of potassium carbonate and sodium carbonate led to lower yields. When organic bases such as DBU and DABCO were used, no reaction occurred. The optimizations of the reaction conditions are summarized in the following section.

Table 1. Hydroamidation of 1-Alkynylphosphine Sulfides[a]

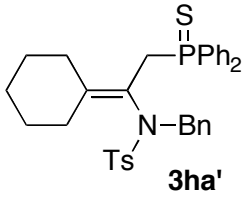


entry	**1**	R^1	**2**	R^2	**3**	yield /%[b]	*E*/*Z*
1	**1a**	Ph	**2a**	Bn[c]	**3aa**	84 (91)	96/4
						71[d]	100/0
2	**1b**	4-Ac-C_6H_4	**2a**	Bn	**3ba**	74	97/3
3	**1c**	4-MeO_2C-C_6H_4	**2a**	Bn	**3ca**	83	95/5
4	**1d**	4-MeO-C_6H_4	**2a**	Bn	**3da**	82[e]	95/5
5	**1e**	2-pyridyl	**2a**	Bn	**3ea**	89	>99/1
6	**1f**	H	**2a**	Bn	**3fa**	88	>99/1
7	**1g**	*n*-C_6H_{13}	**2a**	Bn	**3ga'**	92	87/13
8	**1h**	*c*-C_6H_{11}	**2a**	Bn	**3ha'**	70	
9	**1a**	Ph	**2b**	*n*-C_4H_9	**3ab**	97	96/4
10	**1a**	Ph	**2c**	*c*-C_6H_{11}	**3ac**	15	92/8
11	**1a**	Ph	**2d**	H	**3ad**	23	>99/1

[a] Conditions: **1** (0.50 mmol), **2** (1.0 mmol), Cs_2CO_3 (0.050 mmol), DMSO (3.0 mL), 90 ˚C, 11 h. [b] Isolated yields. NMR yield is in parenthesis. [c] $C_6H_5CH_2$. [d] After recrystallization. [e] The reaction was performed for 24 h.



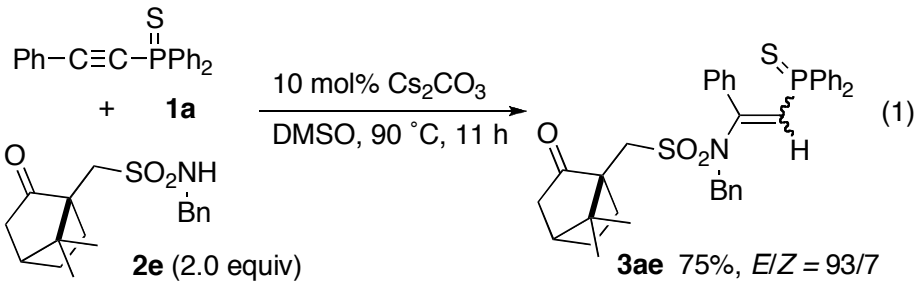
3ga'



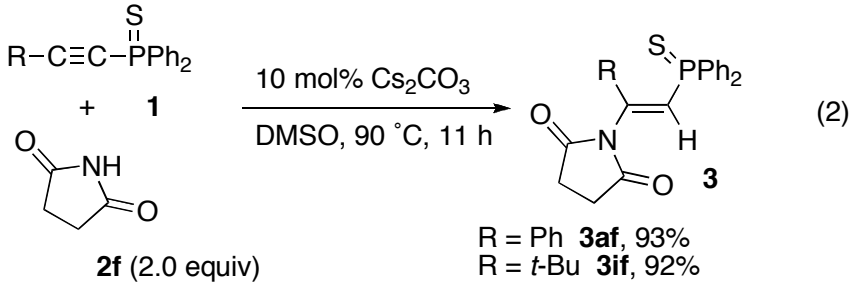
3ha'

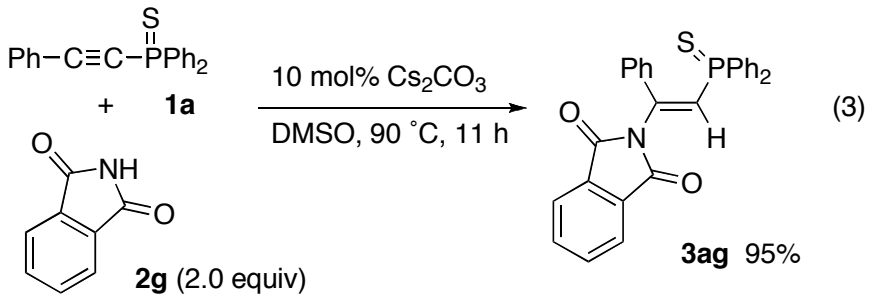
Various combinations of 1-alkynylphosphine sulfides and amides were examined under the optimized reaction conditions (Table 1). A variety of functional groups, such as keto, ester, methoxy, and pyridyl groups, were compatible under the reaction conditions (entries 2–5). The reaction of ethynyldiphenylphosphine sulfide (**1f**) also proceeded smoothly with perfect stereoselectivity (entry 6). However, the reactions of sterically demanding *o*-methoxyphenyl-

and *tert*-butyl-substituted substrates did not take place. The additions to primary and secondary alkyl-substituted 1-alkynylphosphine sulfides also proceeded, although migration of the carbon–carbon double bond occurred to afford **3ga'** and **3ha'** exclusively (entries 7 and 8). The scope of sulfonamides was investigated (entries 9–11). The addition of primary alkyl-substituted tosylamides proceeded in high yields (entries 1 and 9). However, additions of secondary alkyl-substituted tosylamide **2c** and tosylamide (**2d**) provided the corresponding products in low yields (entries 10 and 11), and no reaction occurred when *N*-phenyltosylamide and *N*-*tert*-butyltosylamide were used. The reaction of *N*-benzyl-10-camphorsulfonylamide proceeded smoothly (eq 1).

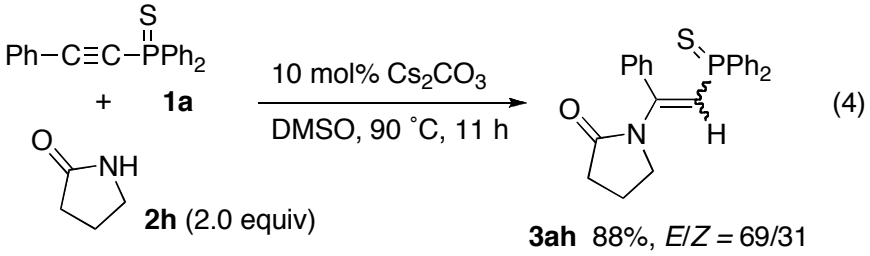


Other nitrogen nucleophiles were examined. Imides were suitable nucleophiles for this addition reaction (eqs 2 and 3). Interestingly, the stereoselectivity was completely controlled when imides were used. In addition, succinimide (**2f**) could react with sterically hindered *tert*-butyl-substituted substrate, with which *N*-benzyltosylamide (**2a**) could not react, and the corresponding adduct was obtained in good yield. The addition of 2-pyrrolidinone also proceeded, albeit with lower stereoselectivity (eq 4). Acyclic amides such as *N*-benzylacetamide did not react at all.



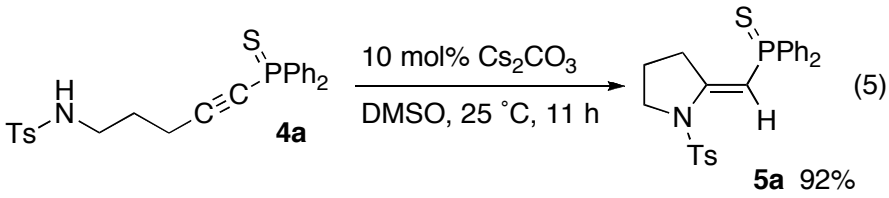


(3)

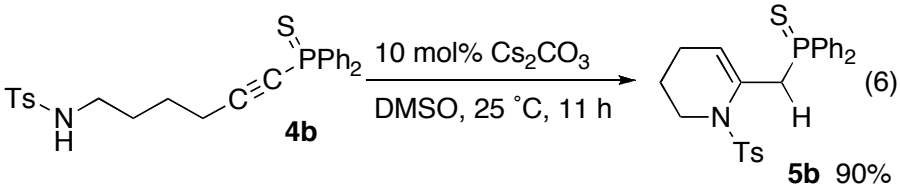


(4)

The amidation was applicable to intramolecular cyclizations. When 1-alkynylphosphine sulfide **4a** which has a tosylamido group was treated with cesium carbonate at ambient temperature, the cyclization proceeded smoothly (eq 5). In the case of eq 6, where tetramethylene-tethered **4b** was used as a substrate, the migration of the C–C double bond of the product occurred.



(5)

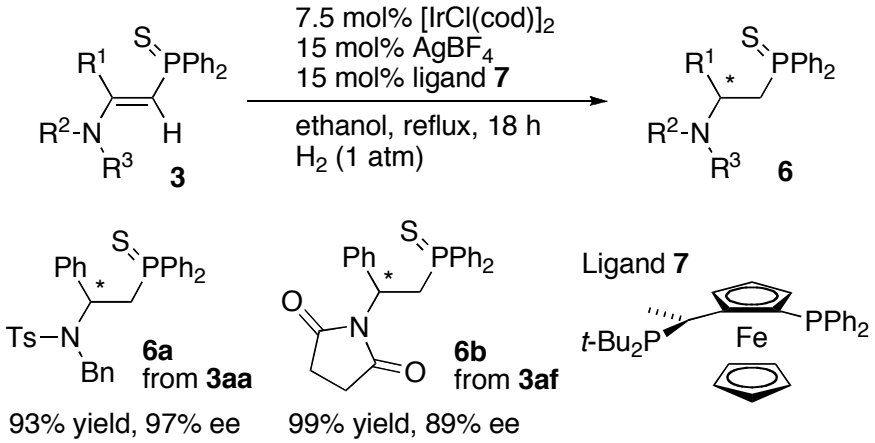


(6)

Enantioselective Hydrogenation of 3. The author envisioned that the enantioselective hydrogenation of the adducts would offer a new approach to chiral bidentate N,P-ligands. However, the enantioselective hydrogenation was not trivial because the adducts are regarded as the sterically demanding and doubly heteroatom-substituted unusual alkenes. After extensive

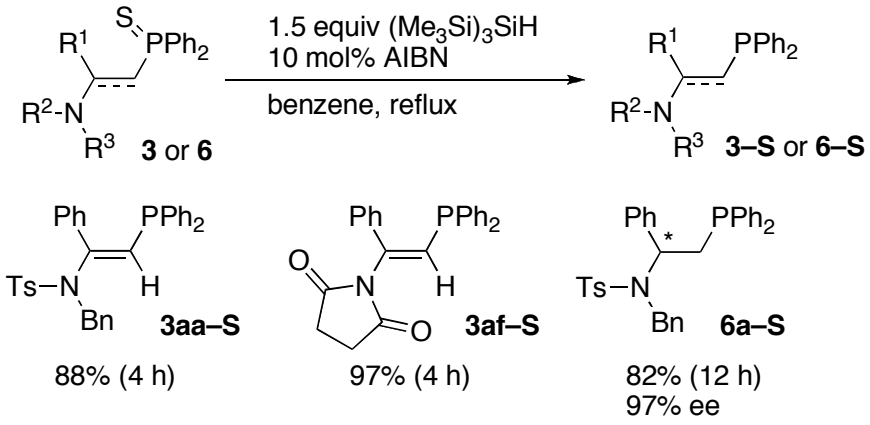
screening of the reaction conditions, he finally found that a combination of a cationic iridium complex[6] and ligand **7**[7] catalyzed the desired reaction with high enantioselectivity (Scheme 1).[8] The hydrogenation of **3aa** in the presence of catalytic amounts of $[IrCl(cod)]_2$, $AgBF_4$, and **7** under 0.1 MPa of hydrogen in boiling ethanol provided **6a** in excellent yield (93%) with 97% ee. The hydrogenation of **3af** was less enantioselective (89% ee), yet high enough to potentially allow for improving the optical purity by recrystallization.

Scheme 1. Iridium-Catalyzed Enantioselective Hydrogenation



Radical Desulfidation of Phosphine Sulfides. Some of the phosphine sulfides thus synthesized were subjected to radical desulfidation conditions[9] to provide the corresponding trivalent phosphines in high yields (Scheme 2). In particular, the optically active phosphine **6a**–**S** would be useful as a ligand after further modifications.

Scheme 2. Desulfidation with TTMSS



Conclusion

The author has found that the cesium-catalyzed hydroamidation of 1-alkynylphosphine sulfides proceeds in good yields with high regio- and stereoselectivities. In light of the importance of organophosphorus compounds, the products and their derivatives can be useful in organic synthesis. In addition, he has demonstrated that the iridium-catalyzed enantioselective hydrogenation of the adducts afforded optically active phosphine sulfides. The protocol, the sequential hydroamidaiton/hydrogenation, offers an alternative to the conventional approach to chiral 2-amino-1-phosphinoalkanes.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to chloroform at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.0 ppm for ^{13}C. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Determination of enantiomeric excess was performed with Shimadzu LCMS-2010A. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. For the preparation of 1-alkynylphosphine, chlorodiphenylphosphine was purchased from TCI. Chlorodicyclohexylphosphine was obtained from Aldrich. Starting 1-alkynylphosphine sulfides **1** were prepared quantitatively by treatment of 1-alkynylphosphines with 3 equiv of crystalline sulfur in THF or DMF with monitoring TLC. Cesium carbonate and chloro(bis-1,5-cyclooctadiene)iridium(I) dimer were purchased from Wako Pure Chemicals. Ligand **7** was available from Strem. Unless otherwise noted, reactions were carried out under argon atmosphere.

Typical Procedure for Hydroamidation of 1-Alkynylphosphine Sulfides

Synthesis of **3aa** is representative. Cs_2CO_3 (0.016 g, 0.050 mmol) was placed in a 20-mL reaction flask under argon. DMSO (3 mL), **1a** (0.16 g, 0.5 mmol), and **2a** (0.26 g, 1.0 mmol) were sequentially added. The resulting solution was heated in an oil bath (90 ˚C) for 11 h. After the mixture was cooled to room temperature, water (10 mL) was added and the product was

extracted with hexane/ethyl acetate (2 : 1, 10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded **3aa** (0.24 g, 0.42 mmol) in 84% yield with *E*/*Z* = 96/4 as a white solid. Recrystallization from hexane/ethyl acetate provided the *E* isomer (0.21 g, 0.36 mmol) exclusively in 71% yield.

Iridium-Catalyzed Enantioselective Hydrogenation

$[IrCl(cod)]_2$ (5.0 mg, 0.0075 mmol), $AgBF_4$ (2.9 mg, 0.015 mmol), and ligand **7** (8.1 mg, 0.015 mmol) were placed in a 20-mL reaction flask under hydrogen. Ethanol (1.0 mL) was added and the mixture was stirred for 1 h. **3aa** (0.058 g, 0.10 mmol) was added and the resulting mixture was heated at reflux for 18 h. After the reaction mixture was cooled to room temperature, filtration through a pad of florisil, concentration, and purification on silica gel yielded **6a** (0.054 g, 0.093 mmol) in 93% yield with 97% ee. HPLC conditions: CHIRALCEL OD-H, hexane/2-propanol = 90:10, 1.5 mL/min, retention time = 9.9 min for the major enantiomer; retention time = 8.1 min for the minor enantiomer. **6b** was synthesized from **3af**, in a fashion similar to the synthesis of **6a** from **3aa**, in 99% yield with 89% ee (0.042 g, 0.099 mmol). HPLC conditions: CHIRALCEL OD-H, hexane/2-propanol = 90:10, 1.5 mL/min, retention time = 8.5 min for the major enantiomer; retention time = 10.3 min for the minor enantiomer.

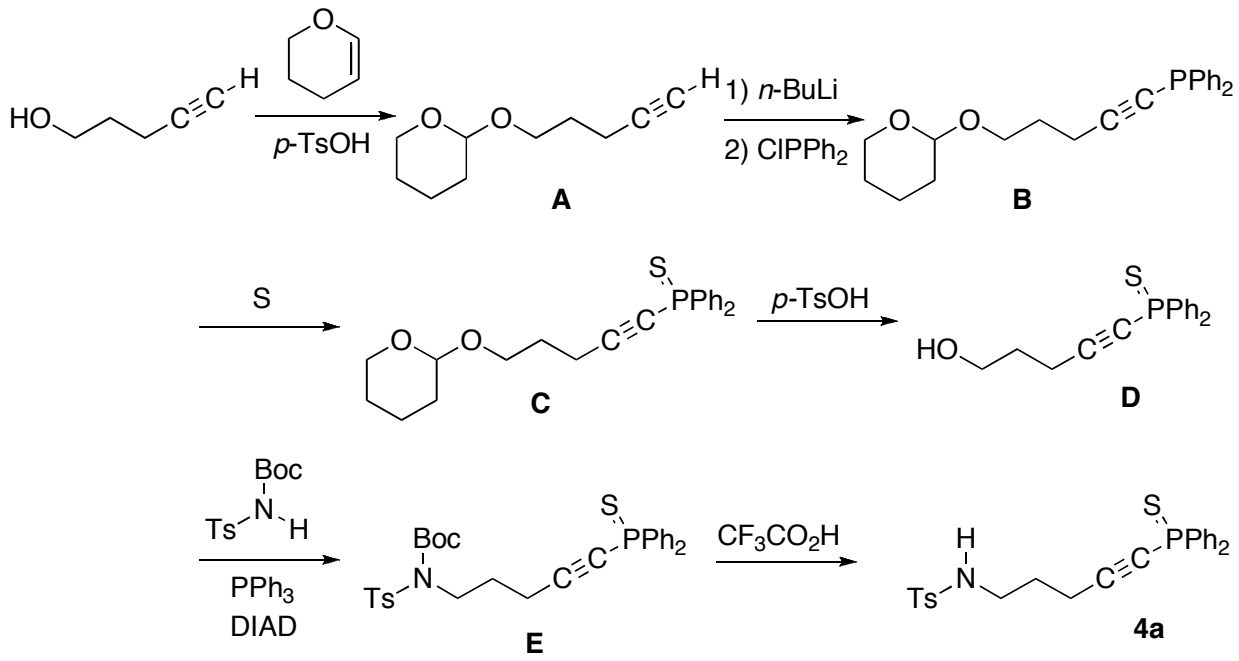
Typical Procedure for the $(Me_3Si)_3SiH$-Mediated Radical Desulfidation Reaction

Synthesis of **6a–S** is representative. AIBN (1.6 mg, 0.010 mmol) and **6a** (0.058 g, 0.10 mmol, 97%ee) were placed in a 20-mL reaction flask under argon. Benzene (2.0 mL) and tris(trimethylsilyl)silane (0.037 g, 0.15 mmol) were sequentially added. The resulting solution was stirred for 12 h at reflux. After being cooled to room temperature, the mixture was concentrated in vacuo. Silica gel column purification provided **6a–S** (0.045 g, 0.082 mmol, 82%, 97% ee). HPLC conditions: CHIRALCEL OD-H, hexane/2-propanol = 98.5:1.5, 1.0

mL/min, retention time = 17.7 min for the major enantiomer; retention time = 15.7 min for the minor enantiomer.

Preparation of 4

Synthesis of **4a** is representative.



Preparation of **A**.

In a 50-mL reaction flask, *p*-TsOH·H_2O (0.19 g, 1.0 mmol) was placed under argon. CH_2Cl_2 (15 mL), 4-pentyn-1-ol (0.84 g, 10 mmol), and 3,4-dihydro-2*H*-pyran (1.0 g, 12 mmol) were sequentially added. The resulting mixture was stirred for 8 h. After water (20 mL) was added, the product was extracted with a hexane/ethyl acetate mixture. Concentration followed by silica gel column purification provided 1.5 g of **A** (9.1 mmol, 91%).

A to **B**.

Under argon, a solution of **A** (1.5 g, 9.1 mmol) in THF (15 mL) was placed in a 50-mL reaction flask. Butyllithium (5.8 mL, 1.6 M in hexane, 9.3 mmol) was added at 0 °C. The resulting mixture was stirred for 30 min at the same temperature. Chlorodiphenylphosphine (2.1

g, 9.5 mmol) was then added at 0 ˚C. The mixture was warmed to room temperature and stirred for 1 h. After water (20 mL) was added, the product was extracted with a hexane/ethyl acetate mixture. Evaporation followed by chromatographic purification afforded **B** (2.8 g, 8.0 mmol, 87%).

B to **C**.

A solution of **B** (2.8 g, 8.0 mmol) in THF (15 mL) was placed in a 50-mL reaction flask under argon. Elemental sulfur (0.27 g, 8.5 mmol) was added, and resulting mixture was stirred for 4 h. Concentration and purification furnished **C** (2.5 g, 6.6 mmol) in 83% yield.

C to **D**.

In a 50-mL reaction flask, *p*-TsOH·H_2O (0.13 g, 0.70 mmol) and a solution of **C** (2.5 g, 6.6 mmol) in ethanol (10 mL) were mixed under argon. The mixture was stirred for 18 h at ambient temperature. Water (20 mL) was added and the product was extracted with ethyl acetate. Evaporation followed by purification on silica gel provided 1.4 g of **D** (4.8 mmol, 73%).

D to **E**.

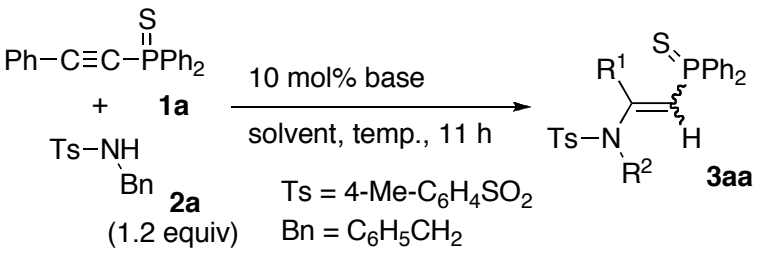
Under argon, a solution of **D** (1.4 g, 4.8 mmol) in THF (40 mL) was placed in a 100-mL reaction flask. PPh_3 (1.26 g, 4.8 mmol) and *N*-Boc-tosylamide (1.3 g, 4.8 mmol) were added. Diisopropyl azodicarboxylate (0.97 g, 4.8 mmol) was added dropwise and the resulting mixture was stirred for 14 h. Water (20 mL) was added and the product was extracted with a hexane/ethyl acetate mixture. Concentration and purification on silica gel provided **E** (1.9 g, 3.4 mmol) in 71% yield.

E to **4a**.

A solution of **E** (1.9 g, 3.4 mmol) in dichloromethane (15 mL) was placed in a 50-mL reaction flask under argon. Trifluoroacetic acid (1.96 g, 17.2 mmol) was added and the mixture was stirred for 18 h. A solution of saturated sodium hydrogen carbonate was added and the product was extracted with a hexane/ethyl acetate mixture. Concentration under reduced pressure followed by chromatographic purification afforded **4a** (1.5 g, 3.4 mmol, 99%).

Optimization of Reaction Conditions

Table 2. Optimization of Reaction Conditions[a]

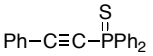


entry	base	solvent	temp. /°C	yield /%[b]	*E*/*Z*
1	Cs_2CO_3	DMSO	90	82	96/4
2	Cs_2CO_3	DMF	90	89	96/4
3	Cs_2CO_3	NMP	90	87	95/5
4	Cs_2CO_3	DMA	90	87	95/5
5	Cs_2CO_3	1,4-dioxane	100	76	97/3
6	Cs_2CO_3	acetonitrile	82	76	94/6
7	Cs_2CO_3	toluene	111	57	94/6
8	Cs_2CO_3	THF	67	7	95/5
9	Cs_2CO_3	*i*-PrOH	82	4	74/26
10	K_2CO_3	DMSO	90	77	95/5
11	Na_2CO_3	DMSO	90	39	93/7
12	DBU	DMSO	90	0	
13	DABCO	DMSO	90	0	

[a] Conditions: **1a** (0.50 mmol), **2a** (0.60 mmol), base (0.050 mmol), solvent (3.0 mL), 11 h. [b] Based on ^{31}P NMR with a sufficient first decay period.

Characterization Data

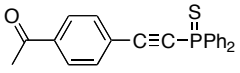
Diphenyl(phenylethynyl)phosphine sulfide (1a)



IR (nujol) 2923, 2854, 2171, 1684, 1653, 1558, 1457, 1436, 1100, 849, 720, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34–7.64 (m, 11H), 7.96–8.06 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 81.96 (d, J = 151.3 Hz), 105.77 (d, J = 25.9 Hz), 120.12 (d, J = 4.3 Hz), 128.48, 128.60 (d, J = 13.9 Hz), 130.57, 130.80 (d, J = 12.4 Hz), 131.74 (d, J = 2.9 Hz), 132.37 (d, J = 2.4 Hz), 133.76 (d, J = 98.4 Hz); ^{31}P NMR ($CDCl_3$) δ 18.39. Found: C, 75.58; H, 4.65%.

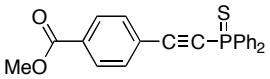
Calcd for $C_{20}H_{15}PS$: C, 75.45; H, 4.75%. m.p.: 108.0–109.5 °C.

(4-Acetylphenylethynyl)diphenylphosphine sulfide (1b)



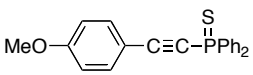
IR (nujol) 2923, 2854, 2176, 1683, 1436, 1266, 1101, 853, 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.59 (s, 3H), 7.44–7.54 (m, 6H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.94–8.02 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.61, 84.79 (d, *J* = 147.4 Hz), 104.01 (d, *J* = 25.4 Hz), 124.49 (d, *J* = 4.3 Hz), 128.14, 128.64 (d, *J* = 13.9 Hz), 130.73 (d, *J* = 12.0 Hz), 131.90 (d, *J* = 2.9 Hz), 132.49 (d, *J* = 2.4 Hz), 133.13 (d, *J* = 98.3 Hz), 137.82, 196.87; ^{31}P NMR ($CDCl_3$) δ 18.65. Found: C, 73.04; H, 4.71%. Calcd for $C_{22}H_{17}OPS$: C, 73.32; H, 4.75%. m.p.: 136.0–137.0 °C.

(4-Methoxycarbonylphenylethynyl)diphenylphosphine sulfide (1c)



IR (nujol) 2924, 2854, 2178, 1718, 1456, 1436, 1377, 1280, 1102, 856, 766, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91 (s, 3H), 7.45–7.55 (m, 6H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.95–8.10 (m, 4H), 8.03 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 52.33, 84.58 (d, *J* = 147.5 Hz), 104.11 (d, *J* = 25.3 Hz), 124.44 (d, *J* = 3.9 Hz), 128.65 (d, *J* = 13.9 Hz), 129.46, 130.76 (d, *J* = 11.9 Hz), 131.52, 131.89 (d, *J* = 3.4 Hz), 132.28 (d, *J* = 1.9 Hz), 133.21 (d, *J* = 98.4 Hz), 165.88; ^{31}P NMR ($CDCl_3$) δ 18.62. Found: C, 69.95; H, 4.57%. Calcd for $C_{22}H_{17}O_2PS$: C, 70.20; H, 4.55%. m.p.: 107.0–108.0 °C.

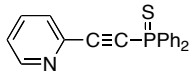
(4-Methoxyphenylethynyl)diphenylphosphine sulfide (1d)



IR (nujol) 2923, 2854, 2170, 1603, 1509, 1436, 1259, 1172, 1101, 1022, 828, 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.81 (s, 3H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.43–7.52 (m, 6H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.96–8.04 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 55.31, 80.54 (d, *J* = 155.1 Hz), 106.52 (d, *J* = 27.3 Hz), 111.83 (d, *J* = 4.4 Hz), 114.11, 128.51 (d, *J* = 13.9 Hz), 130.71 (d, *J* = 11.9 Hz), 131.61 (d, *J* = 2.9 Hz), 133.88 (d, *J* = 97.9 Hz), 134.11 (d, *J* = 1.9 Hz), 161.28; ^{31}P NMR ($CDCl_3$) δ 18.22. Found: C, 72.16; H, 5.12%. Calcd for

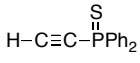
$C_{21}H_{17}OPS$: C, 72.40; H, 4.92%. m.p.: 92.0–93.5 °C.

Diphenyl(2-pyridylethynyl)phosphine sulfide (1e)



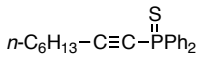
IR (nujol) 2924, 2855, 1558, 1506, 1457, 1097, 865, 782, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (dd, *J* = 4.0, 7.5 Hz, 1H), 7.40–7.54 (m, 6H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 7.5, 8.0 Hz, 1H), 7.94–8.05 (m, 4H), 8.63 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 81.28 (d, *J* = 144.6 Hz), 103.25 (d, *J* = 23.9 Hz), 124.66, 128.48 (d, *J* = 1.0 Hz), 128.63 (d, *J* = 13.8 Hz), 130.84 (d, *J* = 12.4 Hz), 131.89 (d, *J* = 2.9 Hz), 132.96 (d, *J* = 98.4 Hz), 136.29, 140.75 (d, *J* = 4.3 Hz), 150.31; ^{31}P NMR ($CDCl_3$) δ 18.99. Found: C, 71.21; H, 4.29%. Calcd for $C_{19}H_{14}NPS$: C, 71.46; H, 4.42%. m.p.: 113.5–115.0 °C.

Ethynyl(diphenyl)phosphine sulfide (1f)



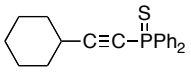
IR (neat) 3221, 3055, 2055, 1479, 1437, 1309, 1104, 1027, 999, 826, 714 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.45 (d, *J* = 10.0 Hz, 1H), 7.45–7.55 (m, 6H), 7.90–7.97 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 78.16 (d, *J* = 141.8 Hz), 94.37 (d, *J* = 23.9 Hz), 128.69 (d, *J* = 13.9 Hz), 130.82 (d, *J* = 12.4 Hz), 132.03 (d, *J* = 2.9 Hz), 132.69 (d, *J* = 97.9 Hz); ^{31}P NMR ($CDCl_3$) δ 18.78. Found: C, 69.14; H, 4.37%. Calcd for $C_{14}H_{11}PS$: C, 69.40; H, 4.58%.

1-Octynyldiphenylphosphine sulfide (1g)



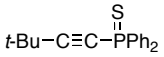
IR (neat) 2930, 2857, 2193, 1437, 1103, 1027, 999, 747, 720, 619, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.22–1.34 (m, 4H), 1.36–1.46 (m, 2H), 1.62 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.46 (dt, *J* = 3.5, 7.5 Hz, 2H), 7.39–7.49 (m, 6H), 7.89–7.97 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.80, 19.87 (d, *J* = 2.9 Hz), 22.27, 27.38 (d, *J* = 1.9 Hz), 28.35, 30.94, 73.80 (d, *J* = 157.0 Hz), 110.16 (d, *J* = 26.3 Hz), 128.35 (d, *J* = 13.9 Hz), 130.56 (d, *J* = 12.4 Hz), 131.43 (d, *J* = 3.4 Hz), 134.00 (d, *J* = 97.9 Hz); ^{31}P NMR ($CDCl_3$) δ 17.55. Found: C, 73.81; H, 7.18%. Calcd for $C_{20}H_{23}PS$: C, 73.59; H, 7.10%.

(Cyclohexylethynyl)diphenylphosphine sulfide (1h)



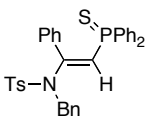
IR (nujol) 2929, 2855, 2185, 1559, 1439, 1311, 1098, 990, 842, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–1.41 (m, 3H), 1.46–1.65 (m, 3H), 1.67–1.78 (m, 2H), 1.83–1.94 (m, 2H), 2.63–2.72 (m, 1H), 7.42–7.51 (m, 6H), 7.89–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 24.57, 25.54, 30.00 (d, J = 2.4 Hz), 31.41 (d, J = 1.5 Hz), 73.60 (d, J = 157.5 Hz), 113.63 (d, J = 25.9 Hz), 128.50 (d, J =13.4 Hz), 130.68 (d, J = 12.0 Hz), 131.52 (d, J = 2.9 Hz), 134.24 (d, J = 97.9 Hz); ^{31}P NMR ($CDCl_3$) δ 17.41. Found: C, 73.87; H, 6.59%. Calcd for $C_{20}H_{21}PS$: C, 74.04; H, 6.52%. m.p.: 104.5–105.5 °C.

(3,3-Dimethyl-1-butynyl)diphenylphosphine sulfide (1i)



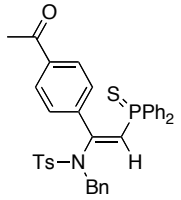
IR (nujol) 2922, 2853, 2158, 1684, 1653, 1558, 1506, 1457, 1437, 1250, 1096, 752, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9H), 7.41–7.51 (m, 6H), 7.88–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.69 (d, J = 2.9 Hz), 29.98 (d, J = 1.9 Hz), 72.31 (d, J = 157.0 Hz), 117.02 (d, J = 24.9 Hz), 128.51 (d, J = 13.9 Hz), 130.69 (d, J = 11.9 Hz), 131.50 (d, J = 3.3 Hz), 134.43 (d, J = 97.9 Hz); ^{31}P NMR ($CDCl_3$) δ 17.28. m.p.: 136.0–137.5 °C.

(*E*)-1-(*N*-Benzyl-*N*-tosylamino)-2-diphenylthiophosphinyl-1-phenylethene (3aa)



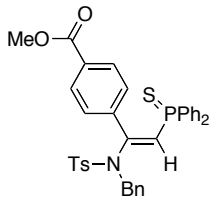
IR (nujol) 2922, 2854, 1559, 1458, 1439, 1359, 1170, 1099, 956, 812, 751, 716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 4.50 (s, 2H), 6.30 (d, J = 13.0 Hz, 1H), 6.93 (dd, J = 7.5, 7.5 Hz, 2H), 7.01–7.07 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 7.19–7.33 (m, 11H), 7.60 (d, J = 8.0 Hz, 2H), 7.62–7.69 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.56, 52.33, 119.49 (d, J = 86.4 Hz), 127.65, 127.66, 127.82, 128.03 (d, J = 12.4 Hz), 128.44, 128.53, 129.74, 129.76 (d, J = 5.3 Hz), 130.12, 130.87 (d, J = 2.9 Hz), 131.29 (d, J = 10.5 Hz), 132.80 (d, J = 86.9 Hz), 133.83 (d, J = 3.4 Hz), 135.75, 136.90, 144.10, 151.43 (d, J = 8.1 Hz); ^{31}P NMR ($CDCl_3$) δ 29.15. Found: C, 70.33; H, 5.18%. Calcd for $C_{34}H_{30}NO_2PS_2$: C, 70.44; H, 5.22%. m.p.: 134.0–135.0 °C.

(*E*)-1-(4-Acetylphenyl)-1-(*N*-benzyl-*N*-tosylamino)-2-diphenylthiophosphinylethene (3ba)



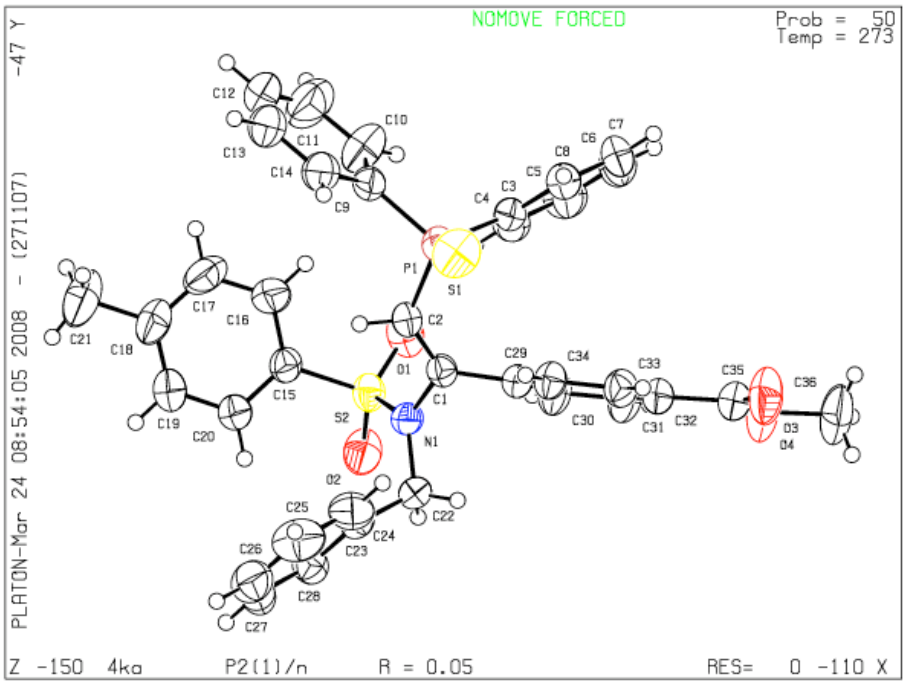
IR (nujol) 2923, 2855, 1674, 1569, 1436, 1360, 1271, 1169, 1092, 957, 849, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 2.47 (s, 3H), 4.50 (s, 2H), 6.36 (d, *J* = 12.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.18–7.33 (m, 13H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.55–7.63 (m, 4H), 7.65 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.61, 26.60, 52.47, 121.43 (d, *J* = 84.4 Hz), 127.39, 127.67, 128.01, 128.11 (d, *J* = 13.0 Hz), 128.48, 128.64, 129.89, 130.28, 131.05 (d, *J* = 2.9 Hz), 131.26 (d, *J* = 10.5 Hz), 132.47 (d, *J* = 86.9 Hz), 135.24, 136.24, 137.38, 138.72 (d, *J* = 3.4 Hz), 144.44, 149.86 (d, *J* = 7.6 Hz), 197.36; ^{31}P NMR ($CDCl_3$) δ 28.89. Found: C, 69.71; H, 5.27%. Calcd for $C_{36}H_{32}NO_3PS_2$: C, 69.54; H, 5.19%. m.p.: 139.0–140.5 °C.

(*E*)-1-(*N*-Benzyl-*N*-tosylamino)-1-(4-methoxycarbonylphenyl)-2-diphenylthiophosphinylethene (3ca)

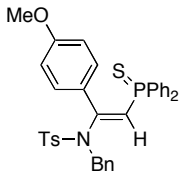


IR (nujol) 2923, 2854, 1719, 1653, 1559, 1507, 1437, 1345, 1274, 1158, 1048, 813, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 3.87 (s, 3H), 4.48 (s, 2H), 6.38 (d, *J* = 12.5 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.19–7.33 (m, 13H), 7.55–7.67 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 21.60, 52.16, 52.42, 121.48 (d, *J* = 84.5 Hz), 127.65, 127.98, 128.12 (d, *J* = 12.4 Hz), 128.45, 128.62, 128.71, 129.88, 130.07, 130.75, 131.07 (d, *J* = 2.9 Hz), 131.26 (d, *J* = 10.9 Hz), 132.53 (d, *J* = 86.9 Hz), 135.27, 136.42, 138.45 (d, *J* = 3.4 Hz), 144.39, 149.99 (d, *J* = 7.6 Hz), 166.28; ^{31}P NMR ($CDCl_3$) δ 28.72. Found: C, 68.08; H, 5.13%. Calcd for $C_{36}H_{32}NO_4PS_2$: C, 67.80; H, 5.06%. m.p.: 156.5–158.0 °C. CCDC No.: 682521.

Figure 1. ORTEP diagram of **3ca**

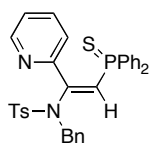


(*E*)-1-(*N*-Benzyl-*N*-tosylamino)-1-(4-methoxyphenyl)-2-diphenylthiophosphinylethene (3da)



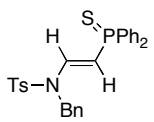
IR (nujol) 2923, 2854, 1559, 1507, 1457, 1340, 1254, 1175, 840, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 3.67 (s, 3H), 4.52 (s, 2H), 6.14 (d, *J* = 13.5 Hz, 1H), 6.45 (d, *J* = 9.0 Hz, 2H), 7.02–7.08 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.18–7.33 (m, 11H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.63–7.70 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.55, 52.39, 55.19, 113.11, 118.17 (d, *J* = 86.9 Hz), 126.36 (d, *J* = 3.9 Hz), 127.61, 127.79, 128.00 (d, *J* = 12.9 Hz), 128.48, 128.52, 129.70, 130.82 (d, *J* = 2.9 Hz), 131.34 (d, *J* = 11.0 Hz), 131.80, 132.87 (d, *J* = 86.4 Hz), 135.83, 136.99, 144.00, 151.30 (d, *J* = 8.6 Hz), 160.75; ^{31}P NMR ($CDCl_3$) δ 29.40. HRMS (EI^+) (*m*/*z*) Observed: 609.1567 (Δ = +1.0 ppm). Calcd for $C_{35}H_{32}NO_3PS_2$ [M^+]: 609.1561. m.p.: 128.0–129.5 °C.

(*E*)-1-(*N*-Benzyl-*N*-tosylamino)-2-diphenylthiophosphinyl-1-(2-pyridyl)ethene (3ea)



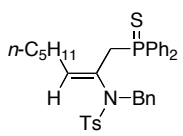
IR (nujol) 2923, 2854, 1458, 1439, 1375, 1357, 1169, 1099, 962, 718 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 4.59 (s, 2H), 6.20 (d, *J* = 12.0 Hz, 1H), 6.84 (dd, *J* = 5.5, 7.5 Hz, 1H), 7.14–7.36 (m, 14H), 7.50–7.62 (m, 5H), 7.78 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.56, 52.80, 122.08 (d, *J* = 84.0 Hz), 123.58, 126.14, 127.89, 127.94 (d, *J* = 12.9 Hz), 128.24, 128.53, 128.68, 129.47, 130.73 (d, *J* = 2.9 Hz), 131.11 (d, *J* = 10.5 Hz), 133.05 (d, *J* = 87.9 Hz), 135.17, 135.25, 135.31, 144.00, 148.43, 148.71 (d, *J* = 6.3 Hz), 152.10 (d, *J* = 3.4 Hz); ^{31}P NMR ($CDCl_3$) δ 31.16. Found: C, 68.05; H, 5.26%. Calcd for $C_{33}H_{29}N_2O_2PS_2$: C, 68.25; H, 5.03%. m.p.: 152.0–153.5 ˚C.

(*E*)-1-(*N*-Benzyl-*N*-tosylamino)-2-diphenylthiophosphinylethene (3fa)



IR (nujol) 2923, 2854, 1598, 1456, 1437, 1353, 1168, 1089, 1048, 762, 712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 4.72 (s, 2H), 5.18 (dd, *J* = 15.0, 15.0 Hz, 1H), 7.25–7.36 (m, 11H), 7.38–7.47 (m, 6H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.74 (dd, *J* = 15.0, 17.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.61, 49.87, 99.53 (d, *J* = 94.5 Hz), 126.94, 127.20, 127.81, 128.40 (d, *J* = 12.5 Hz), 128.95, 130.18, 131.08 (d, *J* = 11.0 Hz), 131.20 (d, *J* = 2.9 Hz), 134.04 (d, *J* = 86.9 Hz), 134.39, 135.42, 142.34 (d, *J* = 18.1 Hz), 144.78; ^{31}P NMR ($CDCl_3$) δ 34.29. Found: C, 66.87; H, 5.32%. Calcd for $C_{28}H_{26}NO_2PS_2$: C, 66.78; H, 5.20%. m.p.: 163.5–164.5 ˚C.

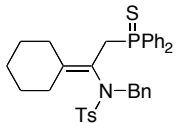
(*E*)-2-(*N*-Benzyl-*N*-tosylamino)-1-diphenylthiophosphinyl-2-octene (3ga')



IR (neat) 3033, 2921, 2852, 1598, 1497, 1434, 1213, 1097, 801 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.5 Hz, 3H), 1.03–1.25 (m, 6H), 2.01–2.08 (m, 2H), 2.34 (s, 3H), 3.93 (d, *J* = 13.0 Hz, 2H), 3.96 (s, 2H), 4.82 (dt, *J* = 5.0, 8.0 Hz, 1H), 7.10–7.21 (m, 7H), 7.44–7.55 (m, 8H), 8.01–8.10 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.86, 21.32, 22.29, 28.25 (d, *J* = 2.4 Hz), 28.72 (d, *J* = 2.4 Hz), 31.09, 37.41 (d, *J* = 51.5 Hz), 53.78, 127.54, 127.75, 127.80, 128.54 (d, *J* = 11.9 Hz), 128.66 (d, *J* = 10.5 Hz), 128.76, 130.35, 131.07 (d, *J* =

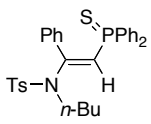
10.0 Hz), 131.41 (d, *J* = 2.9 Hz), 133.18 (d, *J* = 78.3 Hz), 135.97, 136.19, 142.25 (d, *J* = 10.1 Hz), 142.86; ^{31}P NMR ($CDCl_3$) δ 37.92. Found: C, 69.40; H, 6.51%. Calcd for $C_{34}H_{38}NO_2PS_2$: C, 69.48; H, 6.52%.

1-(*N*-Benzyl-*N*-tosylamino)-1-cyclohexylidene-2-diphenylthiophosphinylethane (3ha')



IR (nujol) 2921, 2852, 1558, 1437, 1155, 1093, 1016, 897, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.63–0.73 (m, 1H), 0.76–0.86 (m, 1H), 1.16–1.36 (m, 3H), 1.37–1.50 (m, 2H), 1.54–1.64 (m, 1H), 1.97–2.06 (m, 1H), 2.19–2.29 (m, 1H), 2.44 (s, 3H), 3.50 (d, *J* = 14.5 Hz, 1H), 3.70 (dd, *J* = 15.0, 15.0 Hz, 1H), 3.92 (dd, *J* = 10.5, 15.0 Hz, 1H), 4.20 (d, *J* = 14.5 Hz, 1H), 7.17–7.24 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.39–7.52 (m, 8H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.77–7.83 (m, 2H), 7.90–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.52, 25.77, 26.42 (d, *J* = 2.3 Hz), 27.34 (d, *J* = 2.0 Hz), 31.10 (d, *J* = 2.4 Hz), 32.29 (d, *J* = 2.9 Hz), 36.54 (d, *J* = 49.8 Hz), 52.28, 118.25 (d, *J* = 10.0 Hz), 127.53, 127.82, 127.96, 128.62 (d, *J* = 11.9 Hz), 128.73 (d, *J* = 12.0 Hz), 129.40, 130.32 (d, *J* = 9.5 Hz), 130.53, 131.16 (d, *J* = 2.9 Hz), 131.46 (d, *J* = 10.0 Hz), 131.55 (d, *J* = 2.9 Hz), 132.79 (d, *J* = 75.9 Hz), 135.77 (d, *J* = 78.8 Hz), 136.63, 138.01, 143.14, 152.05 (d, *J* = 9.0 Hz); ^{31}P NMR ($CDCl_3$) δ 38.23. Found: C, 69.34; H, 6.17%. Calcd for $C_{34}H_{36}NO_2PS_2$: C, 69.72; H, 6.19%. m.p.: 68.0–70.0 ˚C.

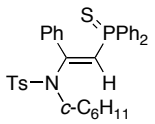
(*E*)-1-(*N*-Butyl-*N*-tosylamino)-2-diphenylthiophosphinyl-1-phenylethene (3ab)



IR (nujol) 2924, 2853, 1559, 1507, 1457, 1437, 1340, 1152, 786 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.74 (t, *J* = 7.5 Hz, 3H), 1.11 (qt, *J* = 7.5, 7.5 Hz, 2H), 1.40 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.43 (s, 3H), 3.27 (t, *J* = 7.5 Hz, 2H), 6.47 (d, *J* = 13.5 Hz, 1H), 6.97 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.04 (t, *J* = 7.0 Hz, 1H), 7.20–7.33 (m, 8H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.75–7.83 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.47, 19.59, 21.56, 30.74, 48.28, 119.79 (d, *J* = 85.4 Hz), 127.54, 127.79, 128.07 (d, *J* = 12.9 Hz), 129.80, 129.82, 130.02, 130.90 (d, *J* = 2.9 Hz), 131.34 (d, *J* = 10.5 Hz), 132.78 (d, *J* = 86.4 Hz), 133.73 (d, *J* = 3.4 Hz), 137.47, 143.99, 151.08 (d, *J* = 8.1 Hz); ^{31}P NMR ($CDCl_3$) δ 28.93. Found: C, 68.28; H, 5.89%.

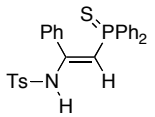
Calcd for $C_{31}H_{32}NO_2PS_2$: C, 68.23; H, 5.91%. m.p.: 129.0–130.5 °C.

(*E*)-1-(*N*-Cyclohexyl-*N*-tosylamino)-2-diphenylthiophosphinyl-1-phenylethene (3ac)



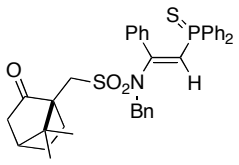
IR (nujol) 2923, 2855, 1558, 1439, 1329, 1288, 1153, 1093, 1039, 887 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.65–1.70 (m, 10H), 2.37 (s, 3H), 3.80–3.90 (m, 1H), 6.07 (d, *J* = 13.5 Hz, 1H), 6.94–7.04 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.23–7.36 (m, 6H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.0 Hz, 2H), 7.79–7.88 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.48, 24.79, 26.28, 32.74, 61.14, 124.07 (d, *J* = 80.1 Hz), 126.95, 127.45, 128.13 (d, *J* = 12.9 Hz), 129.77, 129.90, 130.34, 131.05 (d, *J* = 2.9 Hz), 131.45 (d, *J* = 10.5 Hz), 131.61 (d, *J* = 86.4 Hz), 137.25 (d, *J* = 2.5 Hz), 138.50, 143.51, 149.46 (d, *J* = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ 29.08. HRMS (EI$^+$) (*m/z*) Observed: 571.1768 (Δ = –0.1 ppm). Calcd for $C_{33}H_{34}NO_2PS_2$ [M^+]: 571.1769. m.p.: 190.5–192.5 °C.

(*E*)-2-Diphenylthiophosphinyl-1-phenyl-1-(*N*-tosylamino)ethene (3ad)



IR (nujol) 2923, 2854, 1560, 1507, 1457, 1377, 1344, 1166, 747, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H), 5.30 (d, *J* = 16.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.30–7.50 (m, 13H), 7.53–7.63 (m, 4H), 11.14 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.57, 100.31 (d, *J* = 85.5 Hz), 127.68, 127.87, 128.59, 128.60 (d, *J* = 12.9 Hz), 129.12, 130.45, 130.78 (d, *J* = 10.9 Hz), 131.43 (d, *J* = 2.9 Hz), 133.89 (d, *J* = 87.8 Hz), 136.11, 136.79 (d, *J* = 11.9 Hz), 143.52, 156.24; ^{31}P NMR ($CDCl_3$) δ 26.00. Found: C, 66.14; H, 4.94%. Calcd for $C_{27}H_{24}NO_2PS_2$: C, 66.24; H, 4.94%. m.p.: 192.0–193.5 °C.

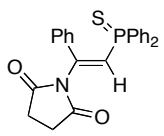
(*E*)-1-[*N*-Benzyl-*N*-{(1*S*)-(+)-10-camphorsulfonyl}amino]-2-diphenylthiophosphinyl-1-phenylethene (3ae)



IR (nujol) 2923, 2853, 1749, 1590, 1437, 1348, 1260, 1154, 1097, 1048, 792 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.68 (s, 3H), 1.01 (s, 3H), 1.40–1.50 (m, 1H), 1.65–1.75 (m, 1H), 1.93 (d, *J* = 18.0 Hz, 1H), 2.00–2.10 (m, 2H), 2.30–2.40

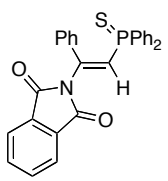
(m, 1H), 2.48–2.58 (m, 1H), 2.66 (d, *J* = 14.0 Hz, 1H), 3.43 (d, *J* = 14.5 Hz, 1H), 4.42 (d, *J* = 15.5 Hz, 1H), 4.49 (d, *J* = 15.5 Hz, 1H), 6.49 (d, *J* = 12.0 Hz, 1H), 7.03 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 7.13–7.38 (m, 11H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.74–7.92 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.49, 19.71, 25.33, 26.91, 42.44, 42.65, 47.74, 52.61, 52.71, 58.62, 119.23 (d, *J* = 86.9 Hz), 127.90, 127.98 (d, *J* = 12.9 Hz), 128.17, 128.20 (d, *J* = 12.4 Hz), 128.79, 128.84, 129.98, 130.32, 130.71 (d, *J* = 2.9 Hz), 130.87 (d, *J* = 2.9 Hz), 131.16 (d, *J* = 11.4 Hz), 131.25 (d, *J* = 11.0 Hz), 132.86 (d, *J* = 85.9 Hz), 133.05 (d, *J* = 86.4 Hz), 133.75 (d, *J* = 3.4 Hz), 135.94, 152.48 (d, *J* = 8.6 Hz), 213.97; ^{31}P NMR ($CDCl_3$) δ 28.28. Found: C, 69.53; H, 6.05%. Calcd for $C_{37}H_{38}NO_3PS_2$: C, 69.46; H, 5.99%. m.p.: 148.0–149.5 °C.

(*E*)-2-Diphenylthiophosphinyl-1-phenyl-1-succinimidoethene (3af)



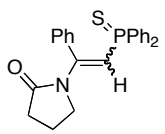
IR (nujol) 2923, 2854, 1718, 1558, 1507, 1457, 1437, 1181, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.71–2.87 (m, 4H), 6.92 (d, *J* = 14.0 Hz, 1H), 7.34–7.43 (m, 5H), 7.45–7.55 (m, 6H), 7.80–7.88 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.96, 119.88 (d, *J* = 80.6 Hz), 126.04, 128.71 (d, *J* = 12.5 Hz), 128.98, 130.68, 131.48 (d, *J* = 11.0 Hz), 131.71 (d, *J* = 2.9 Hz), 133.12 (d, *J* = 89.3 Hz), 135.49 (d, *J* = 11.5 Hz), 145.81 (d, *J* = 2.9 Hz), 175.98; ^{31}P NMR ($CDCl_3$) δ 29.17. Found: C, 68.75; H, 4.90%. Calcd for $C_{24}H_{20}NO_2PS$: C, 69.05; H, 4.83%. m.p.: 199.0–200.0 °C.

(*E*)-2-Diphenylthiophosphinyl-1-phenyl-1-phthalimidoethene (3ag)



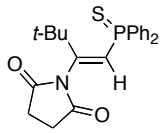
IR (nujol) 2924, 2854, 1740, 1558, 1506, 1456, 1374, 784 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.02 (d, *J* = 12.5 Hz, 1H), 7.29–7.48 (m, 11H), 7.66–7.77 (m, 4H), 7.83–7.91 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 122.42 (d, *J* = 81.1 Hz), 123.72, 126.18, 128.51 (d, *J* = 12.9 Hz), 128.94, 130.54, 131.34 (d, *J* = 2.9 Hz), 131.67 (d, *J* = 11.5 Hz), 131.91, 132.35 (d, *J* = 87.9 Hz), 134.05, 134.35, 136.02 (d, *J* = 12.0 Hz), 142.90 (d, *J* = 3.8 Hz), 166.43; ^{31}P NMR ($CDCl_3$) δ 30.03. Found: C, 72.02; H, 4.20%. Calcd for $C_{28}H_{20}NO_2PS$: C, 72.24; H, 4.33%. m.p.: 172.0–174.0 °C.

2-Diphenylthiophosphinyl-1-phenyl-1-(2-oxopyrrolidino)ethene (3ah) (*E*/*Z* = 69/31)



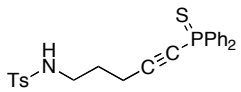
IR (nujol) 2921, 2852, 1700, 1590, 1437, 1378, 1340, 1258, 1098, 887, 753 cm^{-1}; ^1H NMR ($CDCl_3$) (For *E* isomer) δ 1.78 (tt, *J* = 7.0, 8.0 Hz, 2H), 2.13 (t, *J* = 8.0 Hz, 2H), 3.57 (t, *J* = 7.0 Hz, 2H), 6.64 (d, *J* = 14.0 Hz, 1H), 7.35–7.41 (m, 5H), 7.43–7.51 (m, 6H), 7.95–8.02 (m, 4H) (For *Z* isomer) δ 1.97 (tt, *J* = 7.5, 8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 2H), 7.01 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.06 (d, *J* = 14.0 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.20–7.29 (m, 8H), 7.82–7.90 (m, 4H); ^{13}C NMR ($CDCl_3$) (For *E* isomer) δ 18.32, 30.72, 49.52, 118.79 (d, *J* = 84.4 Hz), 126.78, 128.39 (d, *J* = 12.4 Hz), 128.85, 130.24, 131.36 (d, *J* = 3.4 Hz), 131.49 (d, *J* = 11.0 Hz), 132.96 (d, *J* = 87.4 Hz), 135.79 (d, *J* = 12.9 Hz), 149.62 (d, *J* = 2.9 Hz), 175.26 (For *Z* isomer) δ 18.12, 32.66, 49.10, 113.84 (d, *J* = 91.6 Hz), 127.88, 128.04 (d, *J* = 12.4 Hz), 129.23, 129.42, 130.64 (d, *J* = 2.9 Hz), 131.30 (d, *J* = 11.0 Hz), 133.15 (d, *J* = 4.8 Hz), 133.54 (d, *J* = 86.5 Hz), 149.36 (d, *J* = 8.6 Hz), 175.28; ^{31}P NMR ($CDCl_3$) (For *E* isomer) δ 29.38. (For *Z* isomer) δ 28.77. Found: C, 71.74; H, 5.65%. Calcd for $C_{24}H_{22}NOPS$: C, 71.44; H, 5.50%.

(*E*)-1-Diphenylthiophosphinyl-3,3-dimethyl-2-succinimido-1-butene (3if)



IR (nujol) 2925, 2855, 1700, 1539, 1521, 1456, 1363, 1186, 1098, 841, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (s, 9H), 2.62–2.78 (m, 4H), 6.46 (d, *J* = 15.0 Hz, 1H), 7.40–7.52 (m, 6H), 7.71–7.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.85, 28.91, 39.91 (d, *J* = 9.6 Hz), 118.52 (d, *J* = 80.6 Hz), 128.59 (d, *J* = 13.0 Hz), 131.28 (d, *J* = 10.5 Hz), 131.46 (d, *J* = 3.4 Hz), 133.46 (d, *J* = 88.8 Hz), 158.14 (d, *J* = 5.6 Hz), 176.62; ^{31}P NMR ($CDCl_3$) δ 28.41. Found: C, 66.37; H, 6.11%. Calcd for $C_{22}H_{24}NO_2PS$: C, 66.48; H, 6.09%. m.p.: 166.5–167.5 ˚C.

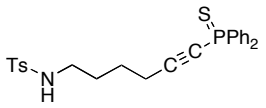
1-Diphenylthiophosphinyl-5-(*N*-tosylamino)-1-pentyne (4a)



IR (nujol) 3200, 2923, 2854, 2197, 1558, 1457, 1439, 1330, 1159, 1072, 716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (tt, *J* = 7.0, 7.0 Hz, 2H), 2.39 (s, 3H), 2.53

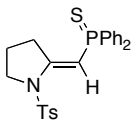
(dt, *J* = 4.0, 7.0 Hz, 2H), 3.04 (dt, *J* = 6.5, 7.0 Hz, 2H), 4.84 (t, *J* = 6.5 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.42–7.52 (m, 6H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.87–7.94 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 17.22 (d, *J* = 3.4 Hz), 21.49, 27.69 (d, *J* = 1.4 Hz), 41.91, 75.03 (d, *J* = 154.3 Hz), 108.25 (d, *J* = 26.3 Hz), 126.98, 128.61 (d, *J* =13.8 Hz), 129.78, 130.73 (d, *J* = 12.0 Hz), 131.73 (d, *J* = 2.9 Hz), 133.66 (d, *J* = 97.9 Hz), 136.65, 143.54; ^{31}P NMR ($CDCl_3$) δ 17.84. Found: C, 63.41; H, 5.54%. Calcd for $C_{24}H_{24}NO_2PS_2$: C, 63.55; H, 5.33%. m.p.: 104.5–105.5 ˚C.

1-Diphenylthiophosphinyl-6-(*N*-tosylamino)-1-hexyne (4b)



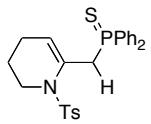
IR (nujol) 3240, 2924, 2855, 2200, 1456, 1437, 1375, 1326, 1163, 1097, 812, 722 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.56–1.68 (m, 4H), 2.40 (s, 3H), 2.44 (dt, *J* = 4.0, 7.0 Hz, 2H), 2.93 (dt, *J* = 6.5, 6.5 Hz, 2H), 4.71 (t, *J* = 6.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.42–7.51 (m, 6H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.86–7.93 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.49 (d, *J* = 3.4 Hz), 21.47, 24.42 (d, *J* = 1.9 Hz), 28.68, 42.39, 74.62 (d, *J* = 155.1 Hz), 109.29 (d, *J* = 26.3 Hz), 127.01, 128.58 (d, *J* =13.9 Hz), 129.71, 130.70 (d, *J* = 12.4 Hz), 131.67 (d, *J* = 3.4 Hz), 133.76 (d, *J* = 97.9 Hz), 136.69, 143.44; ^{31}P NMR ($CDCl_3$) δ 17.76. Found: C, 63.93; H, 5.81%. Calcd for $C_{25}H_{26}NO_2PS_2$: C, 64.22; H, 5.60%. m.p.: 112.5–114.0 ˚C.

2-{(*E*)-2-Diphenylthiophosphinylmethylidene}-1-tosylpyrrolidine (5a)



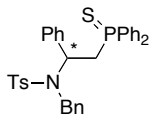
IR (nujol) 2924, 2854, 1606, 1436, 1345, 1270, 1202, 1154, 1065, 1004, 813 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.79 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.45 (s, 3H), 2.73 (t, *J* = 7.5 Hz, 2H), 3.73 (t, *J* = 7.5 Hz, 2H), 6.22 (d, *J* = 15.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.35–7.50 (m, 6H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.71–7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.35, 21.61, 31.37 (d, *J* = 5.3 Hz), 51.23, 94.17 (d, *J* = 98.3 Hz), 127.39, 128.44 (d, *J* = 12.4 Hz), 129.81, 130.89 (d, *J* = 11.0 Hz), 131.04 (d, *J* = 2.9 Hz), 134.31, 135.02 (d, *J* = 86.9 Hz), 144.87, 155.84 (d, *J* = 13.9 Hz); ^{31}P NMR ($CDCl_3$) δ 30.35. Found: C, 63.29; H, 5.34%. Calcd for $C_{24}H_{24}NO_2PS_2$: C, 63.55; H, 5.33%. m.p.: 155.0–156.5 ˚C.

6-Diphenylthiophosphinylmethyl-1-tosyl-2,3,4-trihydropyridine (5b)



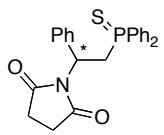
IR (nujol) 2923, 2854, 1456, 1438, 1338, 1170, 1151, 1093, 948, 797 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (tt, *J* = 6.0, 7.5 Hz, 2H), 1.76–1.84 (m, 2H), 2.41 (s, 3H), 2.95 (t, *J* = 6.0 Hz, 2H), 4.02 (d, *J* = 13.0 Hz, 2H), 5.71–5.76 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.43–7.53 (m, 6H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.92–8.00 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.79, 21.55, 22.10 (d, *J* = 2.8 Hz), 40.23 (d, *J* = 48.6 Hz), 46.00, 124.14 (d, *J* = 9.6 Hz), 127.43, 128.03 (d, *J* = 10.5 Hz), 128.33 (d, *J* = 11.9 Hz), 129.60, 131.40 (d, *J* = 2.9 Hz), 131.68 (d, *J* = 10.0 Hz), 132.44 (d, *J* =78.9 Hz), 136.27, 143.66; ^{31}P NMR ($CDCl_3$) δ 41.65. Found: C, 64.33; H, 5.38%. Calcd for $C_{25}H_{26}NO_2PS_2$: C, 64.22; H, 5.66%. m.p.: 155.0–157.0 °C.

1-(*N*-Benzyl-*N*-tosylamino)-2-diphenylthiophosphinyl-1-phenylethane (6a)



IR (nujol) 2867, 1582, 1492, 1455, 1286, 1243, 1196, 1171, 1094, 1008, 824 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 2.95–3.05 (m, 1H), 3.18–3.28 (m, 1H), 3.98 (d, *J* = 16.0 Hz, 1H), 4.62 (d, *J* = 16.0 Hz, 1H), 5.54 (dt, *J* = 2.0, 11.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.84 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 7.10–7.16 (m, 2H), 7.18–7.52 (m, 13H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.62–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.47, 36.14 (d, *J* = 51.5 Hz), 49.33, 57.95 (d, *J* = 4.4 Hz), 127.40, 127.55, 127.63, 127.89, 127.93 (d, *J* = 11.9 Hz), 128.35, 128.43, 128.52 (d, *J* = 12.4 Hz), 129.28, 129.49, 130.85 (d, *J* = 2.9 Hz), 130.94 (d, *J* = 10.0 Hz), 131.03 (d, *J* = 10.5 Hz), 131.39 (d, *J* = 2.9 Hz), 131.81 (d, *J* = 80.1 Hz), 133.32 (d, *J* = 82.6 Hz), 134.69, 137.60, 137.75, 143.21; ^{31}P NMR ($CDCl_3$) δ 36.46. HRMS (EI^+) (*m/z*) Observed: 581.1625 (Δ = +2.3 ppm). Calcd for $C_{34}H_{32}NO_2PS_2$ [M^+]: 581.1612. m.p.: 149.0–150.0 °C. $[\alpha]_D^{25} = -105$ (c 0.0020, $CHCl_3$).

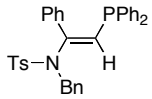
2-Diphenylthiophosphinyl-1-phenyl-1-succinimidoethane (6b)



IR (nujol) 2923, 2854, 1700, 1454, 1437, 1364, 1139, 1101, 743 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.02–2.60 (m, 4H), 2.85–2.95 (m, 1H), 4.40–4.50 (m, 1H), 5.92 (dt, *J* = 2.5, 13.5 Hz, 1H), 7.24–7.31 (m, 3H), 7.43–7.53 (m, 8H), 7.80–7.91 (m, 4H); ^{13}C

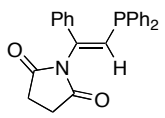
NMR ($CDCl_3$) δ 27.73, 31.49 (d, J = 54.4 Hz), 49.59 (d, J = 1.5 Hz), 127.96, 128.24, 128.45 (d, J = 12.4 Hz), 128.62, 128.73 (d, J = 12.4 Hz), 130.99 (d, J = 10.0 Hz), 131.39 (d, J = 10.5 Hz), 131.52 (d, J = 2.9 Hz), 131.72 (d, J = 2.9 Hz), 132.02 (d, J = 77.4 Hz), 132.34 (d, J = 82.1 Hz), 139.23 (d, J = 12.4 Hz), 176.83; ^{31}P NMR ($CDCl_3$) δ 36.56. HRMS (EI^+) (m/z) Observed: 419.1111 (Δ = +0.6 ppm). Calcd for $C_{24}H_{22}NO_2PS$ [M^+]: 419.1109. m.p.: 63.5–65.0 °C. $[\alpha]_D^{25}$ = –24 (c 0.0050, $CHCl_3$).

(*E*)-1-(*N*-Benzyl-*N*-tosylamino)-2-diphenylphosphino-1-phenylethene (3aa–S)



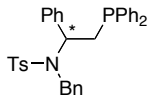
IR (nujol) 2924, 2854, 1590, 1456, 1377, 1311, 1154, 1082, 874, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H), 4.62 (s, 2H), 6.29 (d, J = 4.0 Hz, 1H), 7.05 (d, J = 7.0 Hz, 2H), 7.10 (d, J = 7.5 Hz, 2H), 7.12–7.19 (m, 6H), 7.21–7.35 (m, 12H), 7.58 (d, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.57, 52.17, 126.91 (d, J = 12.9 Hz), 127.64, 127.83 (merged signals), 128.32, 128.34, 128.40 (d, J = 7.6 Hz), 128.95, 129.27, 129.48, 129.51, 132.58 (d, J = 18.6 Hz), 135.55 (d, J = 3.8 Hz), 136.13, 136.72, 139.22 (d, J = 10.0 Hz), 143.54, 149.05 (d, J = 32.5 Hz); ^{31}P NMR ($CDCl_3$) δ –25.53. Found: C, 74.83; H, 5.58%. Calcd for $C_{34}H_{30}NO_2PS$: C, 74.57; H, 5.52%. m.p.: 131.5–132.5 °C.

(*E*)-2-Diphenylphosphino-1-phenyl-1-succinimidoethene (3af–S)



IR (nujol) 2924, 2855, 1719, 1560, 1457, 1375, 1178, 764, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.50–2.82 (m, 4H), 7.01 (d, J = 1.5 Hz, 1H), 7.30–7.39 (m, 11H), 7.46–7.53 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.50, 125.47, 128.67 (d, J = 7.3 Hz), 128.76, 129.05, 129.21, 129.36, 133.18 (d, J = 19.5 Hz), 135.56 (d, J = 3.9 Hz), 136.50 (d, J = 8.6 Hz), 141.51 (d, J = 17.6 Hz), 175.53; ^{31}P NMR ($CDCl_3$) δ –22.08. Found: C, 74.51; H, 5.34%. Calcd for $C_{24}H_{20}NO_2P$: C, 74.80; H, 5.23%. m.p.: 178.5–179.5 °C.

1-(*N*-Benzyl-*N*-tosylamino)-2-diphenylphosphino-1-phenylethane (6a–S)



IR (nujol) 2823, 2854, 1598, 1455, 1377, 1337, 1157, 1091, 1046, 923, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.42 (s, 3H), 2.56–2.68 (m, 2H), 3.92 (d, *J* = 16.0 Hz, 1H), 4.60 (d, *J* = 16.0 Hz, 1H), 4.74–4.82 (m, 1H), 6.86 (d, *J* = 7.5 Hz, 2H), 7.13–7.31 (m, 17H), 7.32–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.50, 32.34 (d, *J* = 15.8 Hz), 48.32, 59.05 (d, *J* = 21.0 Hz), 127.30, 127.32, 128.19, 128.21 (merged signals), 128.26, 128.32 (d, *J* = 6.3 Hz), 128.35, 128.43 (d, *J* = 7.1 Hz), 129.00, 129.17 (d, *J* = 2.4 Hz), 129.40, 132.17 (d, *J* = 18.6 Hz), 133.58 (d, *J* = 20.0 Hz), 136.35 (d, *J* = 2.0 Hz), 137.05 (d, *J* = 14.9 Hz), 137.80, 138.01, 138.17 (d, *J* = 12.4 Hz), 142.98; ^{31}P NMR ($CDCl_3$) δ –24.35. HRMS (EI^+) (*m/z*) Observed: 549.1888 (Δ = –0.5 ppm). Calcd for $C_{34}H_{32}NO_2PS$ [M^+]: 549.1891. m.p.: 43.0–45.0 °C. $[\alpha]_D^{25}$ = –6.0 (c 0.0635, $CHCl_3$)

References and Notes

(1) (a) Rönnholm, P.; Södergren, M.; Hilmersson, G. *Org. Lett.* **2007**, *9*, 3781–3783. (b) Krauss, I. J.; Leighton, J. L. *Org. Lett.* **2003**, *5*, 3201–3203 and references cited therein. (c) Anderson, C.; Cubbon, R. J.; Harling, J. D. *Tetrahedron: Asymmetry* **2001**, *12*, 923–935. (d) Ito, M.; Ikariya, T. *Chem. Commun.* **2007**, 5134–5142.

(2) For recent reviews of catalytic hydroaminations and hydroamidations: (a) Severin, R.; Doya, S. *Chem. Soc. Rev.* **2007**, *36*, 1407–1420. (b) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368–3398. (c) Hong, S.; Marks, T. *Acc. Chem. Res.* **2004**, *37*, 673–686. (d) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675–703. (e) Brunet, J. J.; Neibecker, D. In *Catalytic Heterofunctionallization*; Togni, A., Grutzmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Chapter 4.

(3) For recent examples of intermolecular hydroamidation of alkynes, see: (a) Yudha, S. S.; Kuninobu, Y.; Takai, K. *Org. Lett.* **2007**, *9*, 5609–5611. (b) Gooßen, L. J.; Rauhaus, J. E.; Deng, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 4042–4045. (c) Kondo, T.; Tanaka, S.; Watanabe, Y. *J. Chem. Soc. Chem. Commun.* **1995**, 413–414

(4) For base-mediated additions of tosylamides to propiolates: (a) Barbazanges, M.; Meyer, C.; Cossy, J. *Org. Lett.* **2007**, *9*, 3245–3248. (b) Lee, E.; Kang, T. S.; Joo, B. J.; Tae, J. S.; Li, K. S.; Chung, C. K. *Tetrahedron Lett.* **1995**, *36*, 417–420.

(5) The X-ray crystallographic analysis of **3ca** verified the *E* stereochemistry of the major isomers.

(6) For recent reviews, see: (a) Källström, K.; Munslow, I.; Andersson, P. G. *Chem. –Eur. J.* **2006**, *12*. 3194–3200. (b) Cui, X.; Burgess, K. *Chem. Rev.* **2005**, *105*, 3272–3296.

(7) (a) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tajani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066. (b) Togni, A. *Angew. Chem., Int. Ed.* **1996**, *35*, 1475–1477.

(8) When (*R*)-BINAP was used as a ligand instead of **7**, 91% ee of **6a** was obtained in 82% yield. However, (*R*)-BINAP was less effective for the enantioselective hydrogenation of **3af** to provide **6b** in 99% yield with 15% ee.

(9) Romeo, R.; Wozniak, L. A.; Chatgilialoglu, C. *Tetrahedron Lett*. **2000**, *41*, 9899–9902.

Chapter 4

Synthesis of Bulky Phosphines by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides

Treatment of 1-alkynylphosphine sulfides with 1,6- or 1,7-diynes in the presence of a cationic rhodium catalyst results in a formal [2+2+2] cycloaddition reaction to afford the corresponding aromatic phosphine sulfides. The aromatic rings formed in the cycloaddition naturally bear one or two substituents at the *ortho* positions to the phosphorus atom, which creates a sterically hindered environment around the phosphorus atom. The following desulfidation yields bulky phosphines that will potentially serve as ligands in transition-metal-catalyzed reactions.

Introduction

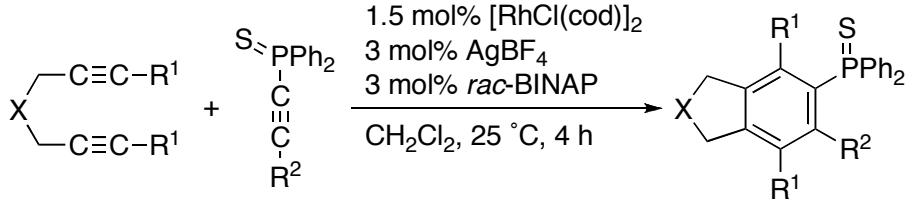
In the modern organic synthesis, bulky phosphine ligands play an indispensable role in preparing biologically interesting compounds as well as organic functional materials.[1] Synthesis of such bulky ligands is hence quite important. However, the methods for the synthesis are mostly limited to the reaction of a chlorophosphine with a bulky organometallic reagent[2] and the transition-metal-catalyzed phosphination or phosphinylation of a bulky aryl halide.[3]

In chapter 4, the author describes a conceptually different approach to bulky phosphines. Rhodium-catalyzed formal [2+2+2] cycloaddition reaction[4] of 1,6-diynes and 1-alkynylphosphine sulfides[5] afforded benzene rings having a thiophosphinyl moiety. When substrates are properly designed, the newly formed benzene rings naturally have one or two substituents next to the thiophosphinyl group, which provide sterically congested environment around the phosphorus.[6,7]

Results and Discussion

The reaction of 1,6-diyne **1a** with 1-octynyldiphenylphosphine sulfide (**2a**) proceeded smoothly in dichloromethane in the presence of a cationic rhodium catalyst and BINAP (Table 1, entry 1). Among the ligands the author screened, BINAP was the best ligand. When DPPE, DPPF, or PPh_3 (2 equiv to Rh) was used, the yield was moderate. The generation of the cationic rhodium species by the action of silver tetrafluoroborate was essential. Without the silver salt, only **1a** participated in the cycloaddition reaction to form dimerized **4a** and no **3aa** was obtained. The cationic rhodium center would induce the strong coordination of **2a**. Iridium catalysis, $[IrCl(cod)]_2$ with or without the silver salt, for instance, left **2a** untouched and provided **4a** instead. The use of [Cp*RuCl(cod)] only promoted the very slow dimerization of **1a**. The reaction of trivalent 1-octynyldiphenylphosphine with **1a** resulted in no conversion. The highly coordinating nature of the trivalent phosphine would cause deactivation of the catalyst. The reaction of 1-octynyldiphenylphosphine oxide with **1a** provided 40% yield of the corresponding product along with **4a**. The sulfide moiety seems to properly assist the reaction of a rhodacyclopentadiene intermediate with **2a** in the catalytic cycle.[8]

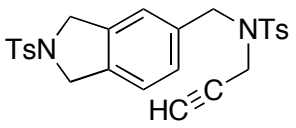
Table 1. Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides[a]



1 (1.2 equiv) **2** **3**

entry	**1**	X[b]	R^1	**2**	R^2	**3**	yield /%[c]
1	**1a**	TsN	H	**2a**	*n*-C_6H_{13}	**3aa**	71
2	**1b**	O	H	**2a**	*n*-C_6H_{13}	**3ba**	77
3	**1c**	E_2C	H	**2a**	*n*-C_6H_{13}	**3ca**	97
4	**1d**	CH_2	H	**2a**	*n*-C_6H_{13}	**3da**	60
5	**1e**	CH_2CH_2	H	**2a**	*n*-C_6H_{13}	**3ea**	93
6	**1c**	E_2C	H	**2b**	Ph	**3cb**	85
7	**1c**	E_2C	H	**2c**	*i*-Pr	**3cc**	83
8	**1c**	E_2C	H	**2d**	*t*-Bu	**3cd**	74
9	**1c**	E_2C	H	**2e**	2-MeO-C_6H_4	**3ce**	85
10	**1c**	E_2C	H	**2f**	Me_3Si	**3cf**	80
11	**1f**	E_2C	Me	**2a**	*n*-C_6H_{13}	**3fa**	87[d]
12	**1g**	E_2C	Ph	**2a**	*n*-C_6H_{13}	**3ga**	90[d]
13	**1g**	E_2C	Ph	**2b**	Ph	**3gb**	65[d,e]
14	**1h**	E_2C	*i*-Pr	**2c**	*i*-Pr	**3hc**	70[d,f]
15	**1h**	E_2C	*i*-Pr	**2g**	2-MeO-Np[g]	**3hg**	77[d,f]

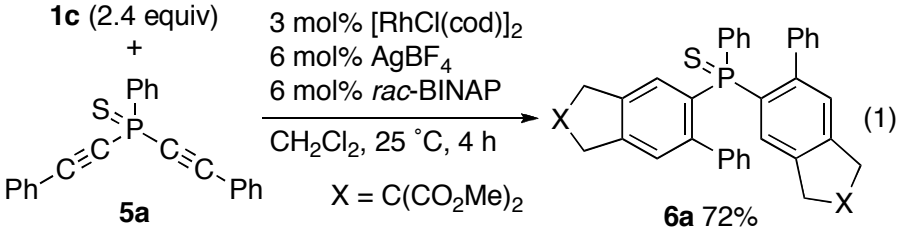
[a] Conditions: **1** (0.60 mmol), **2** (0.50 mmol), $[RhCl(cod)]_2$ (0.0075 mmol), $AgBF_4$ (0.015 mmol), *rac*-BINAP (0.015 mmol), dichloromethane (4.0 mL), 25 ˚C, 4 h. [b] Ts = 4-Me-C_6H_4-SO_2, E = CO_2Me. [c] Isolated yields. [d] The reaction was performed in 1,2-dichloroethane at reflux. [e] The reaction was performed for 12 h. [f] $[RhCl(cod)]_2$ (5 mol%), $AgBF_4$ (10 mol%), *rac*-BINAP (10 mol%), 12 h. [g] 2-Methoxy-1-naphthyl.

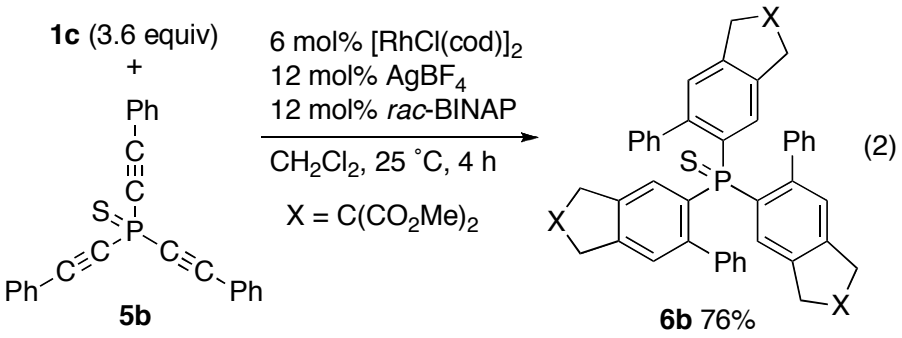


4a

Various combinations of tethered diynes and 1-alkynylphosphine sulfides were examined (Table 1). Dipropargyl ether (**1b**) and a diyne **1c** derived from dimethyl malonate reacted smoothly with **2a**. The latter provided the corresponding triarylphosphine sulfide **3ca** in the highest yield of 97% (entry 3). 1,7-Octadiyne (**1e**) was superior to 1,6-heptadiyne (**1d**) as a substrate.

The scope of 1-alkynylphosphine sulfides (entries 6–10) is wide enough to employ not only phenyl-substituted **2b** but also bulky isopropyl- and *tert*-butyl-substituted **2c** and **2d**. The reactions of *o*-methoxyphenyl-substituted **2e** and trimethylsilyl-substituted **2f** proceeded smoothly. The reaction is so powerful that dialkynylphosphine sulfide **5a** and trialkynylphenylphosphine sulfide **5b** participated in multiple cycloadditions to yield the corresponding products in high yields (eqs 1 and 2).

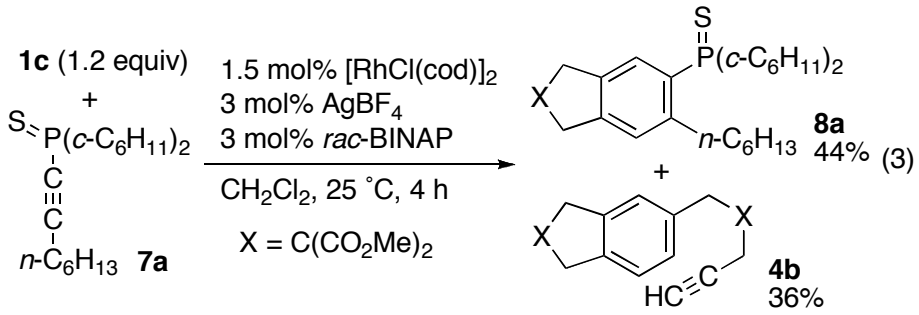


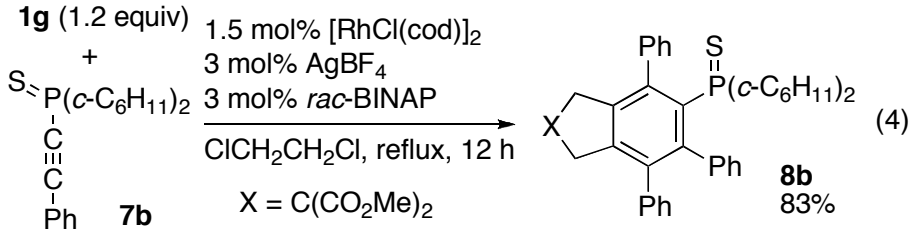


Reactions of internal diynes ($R^1 \neq H$) did not proceed at all in dichloromethane at 25 °C. Instead, performing the reactions in refluxing 1,2-dichloroethane resulted in smooth conversion to afford the corresponding products in good yields (entries 11–15). The products have a 2,6-disubstituted phenyl group on the phosphorus, which creates a considerable steric effect.[9] Interestingly, the reaction of **1h** with diphenyl[(2-methoxy-1-naphthyl)ethynyl]phosphine sulfide

(**2g**) provided phosphine sulfide **3hg**, which has a chiral axis.[10] The use of monosubstituted **1**, where one R^1 is H and the other R^1 is Ph, resulted in self-dimerization of the diyne.

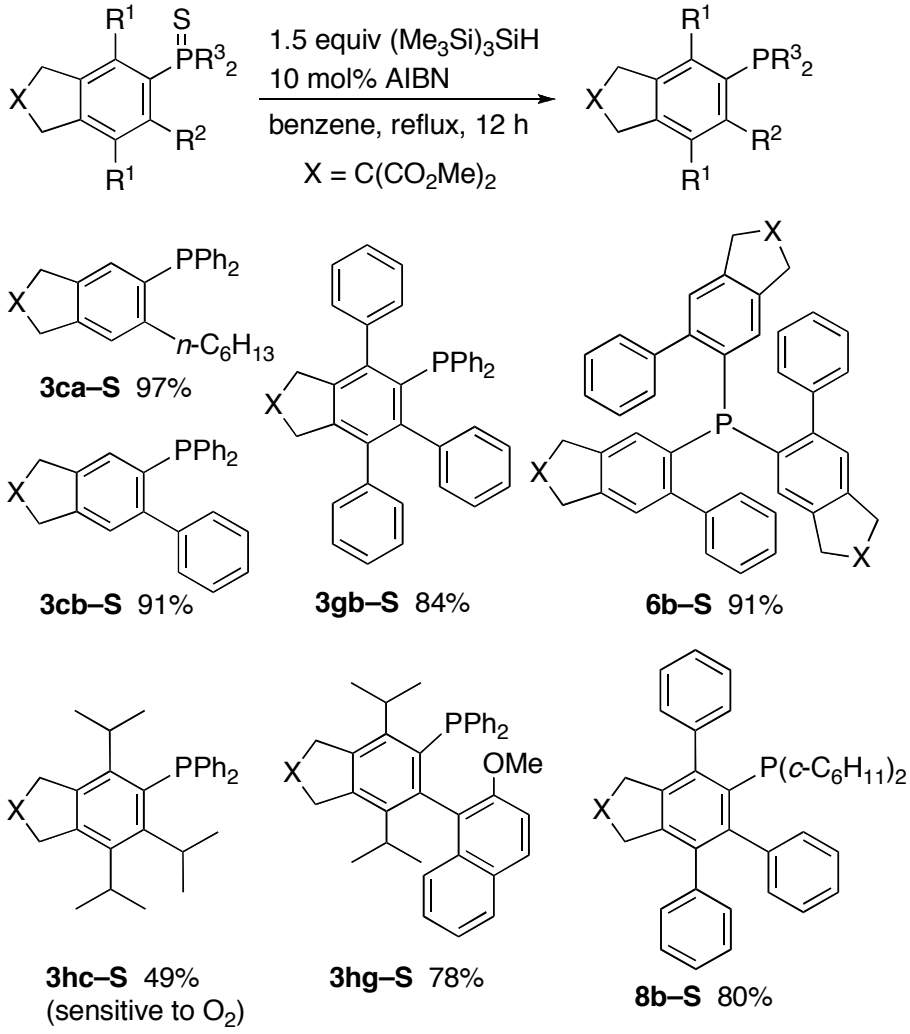
1-Alkynyldicyclohexylphosphine sulfides **7** were less reactive than the corresponding diphenyl analogues **2**. The reaction of terminal diyne **1c** with **7a** provided the desired product **8a** in moderate yield with concomitant formation of **4b** (eq 3). The reaction of internal diyne **1g** with dicyclohexylphosphine sulfide **7b** was successful to yield highly crowded **8b** in high yield (eq 4).



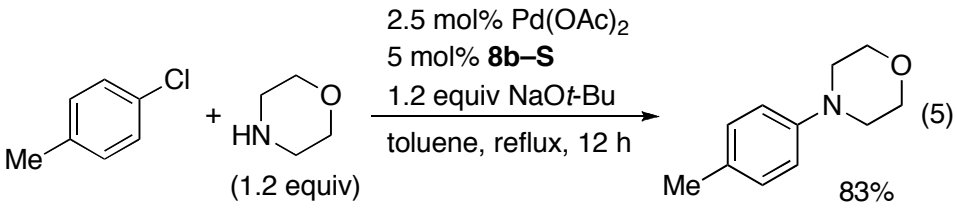


Radical Desulfidation of Phosphine Sulfides. The products, phosphine sulfides, were subjected to radical desulfidation conditions[11] to provide the corresponding trivalent phosphines in high yields (Scheme 1). The desulfidation reactions of these bulky phosphines were clean and high-yielding. Except for triisopropyl-substituted **3hc–S**, the phosphines obtained were stable under air. The author could perform the purification of the trivalent phosphines on silica gel without any special care. The present method offers a novel access to bulky phosphine ligands.

Scheme 1. Desulfidation with TTMSS



Application of Newly Synthesized Bulky Phosphine. Application of the bulky phosphine was examined. The ligand **8b–S** proved to serve as a ligand for the amination of aryl chloride with morpholine (eq 5).[12]



Conclusion

The combination of the rhodium-catalyzed formal cycloaddition of diynes with 1-alkynylphosphine sulfides and subsequent desulfidation of the cycloadducts thus represents a conceptually novel access to bulky phosphines. The bulky phosphine ligands prepared by this method will find many applications in organic synthesis.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to chloroform at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.0 ppm for ^{13}C. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Determination of enantiomeric excess was performed with Shimadzu LCMS-2010A. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. For the preparation of 1-alkynylphosphine, chlorodiphenylphosphine was purchased from TCI. Chlorodicyclohexylphosphine was obtained from Aldrich. Starting 1-alkynylphosphine sulfides **2** were prepared by the methods described in Chapter 3. Chloro(bis-1,5-cyclooctadiene)rhodium(I) dimer was purchased from Wako Pure Chemicals. Silver(I) tetrafluoroborate and racemic BINAP were obtained from Aldrich. Palladium(II) acetate was purchased from TCI. All reactions were carried out under argon atmosphere.

Typical Procedure for the Rhodium-Catalyzed Reaction

Synthesis of **3ca** is representative. $[RhCl(cod)]_2$ (3.7 mg, 0.0075 mmol), $AgBF_4$ (2.9 mg, 0.015 mmol), and BINAP (9.3 mg, 0.015 mmol) were placed in a 20-mL reaction flask under argon. Dichloromethane (4.0 mL), 1-octynyldiphenylphosphine sulfide (**2a**, 0.16 g, 0.50 mmol), and 4,4-di(methoxycarbonyl)-1,6-heptadiyne (**1c**, 0.13 g, 0.60 mmol) were sequentially added. The resulting solution was stirred for 4 h at 25 ˚C. Water (10 mL) was added, and the product

was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded **3ca** (0.26 g, 0.49 mmol, 97%) as a white solid.

Typical Procedure for the $(Me_3Si)_3SiH$-Mediated Radical Desulfidation Reaction

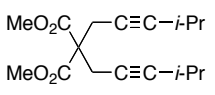
Synthesis of **3gb–S** is representative. AIBN (1.6 mg, 0.010 mmol) and **3gb** (0.068 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. Benzene (2.0 mL) and tris(trimethylsilyl)silane (0.037 g, 0.15 mmol) were sequentially added. The resulting solution was stirred for 12 h at reflux. After being cooled to room temperature, the mixture was concentrated in vacuo. Silica gel column purification provided **3gb–S** (0.054 g, 0.084 mmol, 84%) as a white solid.

Procedure for the Amination of Aryl Chloride with Morpholine (eq 5)

Palladium acetate (2.8 mg, 0.013 mmol), **8b–S** (0.017 g, 0.025 mmol), and sodium *tert*-butoxide were placed in a 20-mL reaction flask under argon. Toluene (3.0 mL) was added, and the mixture was stirred for 10 min. 4-Chlorotoluene and morpholine were sequentially added. The resulting mixture was heated at reflux for 12 h. After the mixture was cooled to room temperature, water (10 mL) was added. Extractive workup with ethyl acetate followed by silica gel column purification provided *N*-(4-methylphenyl)morpholine (0.075g, 0.42 mmol) in 83% yield.

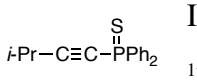
Characterization Data

6,6-Di(methoxycarbonyl)-2,10-dimethyl-3,8-undecadiyne (1h)



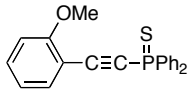
IR (neat) 2970, 2873, 1744, 1436, 1326, 1293, 1210, 1181, 1062, 950, 902, 854 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (d, J = 7.0 Hz, 12H), 2.46 (sept, J = 7.0 Hz, 2H), 2.88 (s, 4H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 20.41, 22.86, 23.16, 52.71, 57.55, 73.42, 89.34, 169.65. Found: C, 68.58; H, 8.23%. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27%.

(3-Methyl-1-butynyl)diphenylphosphine sulfide (2c)



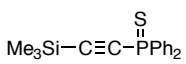
IR (nujol) 2924, 2854, 2187, 1478, 1436, 1311, 1111, 978, 835, 720, 662 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, *J* = 7.0 Hz, 6H), 2.84 (dsept, *J* = 3.5, 7.0 Hz, 1H), 7.42–7.52 (m, 6H), 7.88–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.72 (d, *J* = 3.4 Hz), 21.79 (d, *J* = 1.9 Hz), 72.94 (d, *J* = 33.5 Hz), 114.68 (d, *J* = 25.3 Hz), 128.52 (d, *J* = 13.9 Hz), 130.73 (d, *J* = 12.4 Hz), 131.56 (d, *J* = 2.9 Hz), 134.19 (d, *J* = 99.3 Hz); ^{31}P NMR ($CDCl_3$) δ 17.40. Found: C, 71.58; H, 6.03%. Calcd for $C_{17}H_{17}PS$: C, 71.80; H, 6.03%. m.p.: 80.5–82.0 °C.

(2-Methoxyphenylethynyl)diphenylphosphine sulfide (2e)



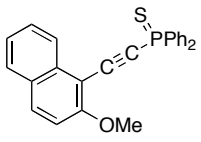
IR (nujol) 2920, 2851, 1773, 1718, 1684, 1653, 1559, 1507, 1457, 1420, 1263, 1024, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91 (s, 3H), 6.90–6.97 (m, 2H), 7.38–7.55 (m, 8H), 8.02–8.10 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 55.84, 85.47 (d, *J* = 155.1 Hz), 103.04 (d, *J* = 27.3 Hz), 109.63 (d, *J* = 4.4 Hz), 110.80, 120.48, 128.52 (d, *J* = 13.4 Hz), 130.93 (d, *J* = 12.4 Hz), 131.58 (d, *J* = 2.9 Hz), 132.17, 134.04 (d, *J* = 2.0 Hz), 134.20 (d, *J* = 98.4 Hz), 161.54; ^{31}P NMR ($CDCl_3$) δ 18.42. Found: C, 72.47; H, 4.97%. Calcd for $C_{21}H_{17}OPS$: C, 72.40; H, 4.92%. m.p.: 77.0–78.5 °C.

(Trimethylsilylethynyl)diphenylphosphine sulfide (2f)



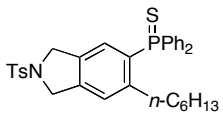
IR (nujol) 2920, 2851, 2401, 1735, 1685, 1560, 1540, 1438, 1252, 1097, 713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.28 (s, 9H), 7.43–7.53 (m, 6H), 7.88–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –0.77, 97.60 (d, *J* = 133.6 Hz), 116.01 (d, *J* = 14.8 Hz), 128.60 (d, *J* = 13.8 Hz), 130.81 (d, *J* = 12.0 Hz), 131.73 (d, *J* = 3.4 Hz), 133.58 (d, *J* = 97.4 Hz); ^{31}P NMR ($CDCl_3$) δ 17.12. Found: C, 64.75; H, 6.25%. Calcd for $C_{17}H_{19}PSSi$: C, 64.93; H, 6.09%. m.p.: 158.0–159.5 °C.

(2-Methoxy-1-naphthylethynyl)diphenylphosphine sulfide (2g)



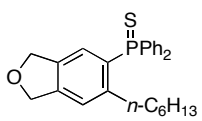
IR (nujol) 2923, 2854, 2333, 2164, 1587, 1460, 1438, 1378, 1277, 1095, 812, 718, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.01 (s, 3H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.34–7.40 (m, 1H), 7.46–7.55 (m, 7H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 8.10–8.20 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 56.49, 90.56 (d, *J* = 155.0 Hz), 102.12 (d, *J* = 27.3 Hz), 102.98, 112.16, 124.51, 124.69, 128.05, 128.19, 128.22, 128.51 (d, *J* = 13.9 Hz), 130.90 (d, *J* = 12.0 Hz), 131.57 (d, *J* = 3.3 Hz), 132.83, 134.33 (d, *J* = 97.9 Hz), 134.44, 161.39 (d, *J* = 1.9 Hz); ^{31}P NMR ($CDCl_3$) δ 18.59. Found: C, 75.10; H, 4.72%. Calcd for $C_{25}H_{19}OPS$: C, 75.36; H, 4.81%. m.p.: 117.5–119.0 ˚C.

(6-Hexyl-*N*-tosyl-5-isoindolinyl)diphenylphosphine sulfide (3aa)



IR (nujol) 2923, 2854, 1597, 1459, 1437, 1378, 1350, 1166, 1099, 695, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.79 (t, *J* = 7.5 Hz, 3H), 0.98–1.07 (m, 4H), 1.10–1.20 (m, 2H), 1.28–1.38 (m, 2H), 2.41 (s, 3H), 2.66–2.74 (m, 2H), 4.43 (s, 2H), 4.60 (s, 2H), 6.76 (d, *J* = 14.5 Hz, 1H), 7.17 (d, *J* = 4.0 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.41–7.55 (m, 6H), 7.70–7.81 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 13.97, 21.47, 22.40, 29.14, 30.81, 31.43, 34.19 (d, *J* = 5.8 Hz), 53.40, 53.58, 125.15 (d, *J* = 11.0 Hz), 126.82 (d, *J* = 13.4 Hz), 127.55, 128.54 (d, *J* = 12.4 Hz), 129.83, 131.58 (d, *J* = 2.9 Hz), 131.66 (d, *J* = 84.9 Hz), 132.20 (d, *J* = 10.0 Hz), 132.66 (d, *J* = 83.5 Hz), 133.38 (d, *J* = 13.9 Hz), 133.55, 140.15 (d, *J* = 2.4 Hz), 143.80, 147.48 (d, *J* = 10.0 Hz); ^{31}P NMR ($CDCl_3$) δ 40.52. Found: C, 68.90; H, 6.29%. Calcd for $C_{33}H_{36}NO_2PS$: C, 69.08; H, 6.32%. m.p.: 189.0–191.0 ˚C.

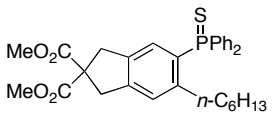
(6-Hexyl-1,3-dihydro-5-isobenzofuranyl)diphenylphosphine sulfide (3ba)



IR (nujol) 2925, 2853, 1684, 1653, 1558, 1437, 1097, 1049, 904, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, *J* = 7.5 Hz, 3H), 1.02–1.10 (m, 4H), 1.11–1.21 (m, 2H), 1.35–1.44 (m, 2H), 2.75–2.82 (m, 2H), 4.94 (s, 2H), 5.09 (s, 2H), 6.86 (d, *J* = 14.5 Hz, 1H), 7.25 (d, *J* = 4.5 Hz, 1H), 7.43–7.55 (m, 6H), 7.78–7.86 (m, 4H); ^{13}C NMR

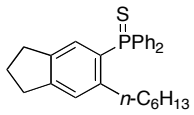
($CDCl_3$) δ 13.97, 22.40, 29.17, 30.88, 31.45, 34.25 (d, *J* = 6.1 Hz), 73.24, 73.28, 123.55 (d, *J* = 11.4 Hz), 125.25 (d, *J* = 13.3 Hz), 128.46 (d, *J* = 12.4 Hz), 132.24 (d, *J* = 85.9 Hz), 131.43 (d, *J* = 2.9 Hz), 132.23 (d, *J* = 10.5 Hz), 132.98 (d, *J* = 83.5 Hz), 136.36 (d, *J* = 13.4 Hz), 143.33 (d, *J* = 2.9 Hz), 147.03 (d, *J* = 10.5 Hz); ^{31}P NMR ($CDCl_3$) δ 40.87. Found: C, 74.00; H, 6.97%. Calcd for $C_{26}H_{29}OPS$: C, 74.26; H, 6.95%. m.p.: 117.5–119.0 ˚C.

[6-Hexyl-2,2-di(methoxycarbonyl)-5-indanyl]diphenylphosphine sulfide (3ca)



IR (nujol) 2923, 2853, 1731, 1654, 1560, 1457, 1430, 1250, 1162, 1120, 1075, 1059, 701, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, *J* = 7.5 Hz, 3H), 1.00–1.10 (m, 4H), 1.11–1.21 (m, 2H), 1.30–1.41 (m, 2H), 2.67–2.73 (m, 2H), 3.44 (s, 2H), 3.59 (s, 2H), 3.74 (s, 6H), 6.79 (d, *J* = 14.5 Hz, 1H), 7.19 (d, *J* = 4.5 Hz, 1H), 7.42–7.54 (m, 6H), 7.76–7.84 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.46, 29.27, 30.89, 31.53, 34.26 (d, *J* = 5.8 Hz), 40.30, 40.60, 53.02, 60.07, 126.83 (d, *J* = 11.4 Hz), 128.44 (d, *J* = 12.0 Hz), 128.47 (d, *J* = 12.9 Hz), 130.11 (d, *J* = 85.9 Hz), 131.36 (d, *J* = 2.9 Hz), 132.33 (d, *J* = 10.5 Hz), 133.19 (d, *J* = 83.5 Hz), 137.04 (d, *J* = 13.8 Hz), 144.20 (d, *J* = 2.9 Hz), 146.57 (d, *J* = 10.0 Hz), 171.83; ^{31}P NMR ($CDCl_3$) δ 40.69. Found: C, 69.44; H, 6.33%. Calcd for $C_{31}H_{35}O_4PS$: C, 69.64; H, 6.60%. m.p.: 159.0–160.5 ˚C.

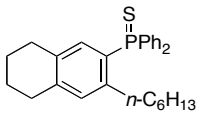
(6-Hexyl-5-indanyl)diphenylphosphine sulfide (3da)



IR (neat) 3054, 2848, 1963, 1898, 1817, 1775, 1675, 1607, 1557, 1436, 1391, 1309, 1097, 998 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, *J* = 7.5 Hz, 3H), 1.00–1.10 (m, 4H), 1.12–1.22 (m, 2H), 1.34–1.44 (m, 2H), 2.03 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 15.0 Hz, 1H), 7.22 (d, *J* = 4.5 Hz, 1H), 7.41–7.53 (m, 6H), 7.79–7.86 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.47, 25.25, 29.30, 31.05, 31.56, 32.47, 32.90, 34.27 (d, *J* = 6.1 Hz), 127.06 (d, *J* = 11.5 Hz), 128.36 (d, *J* = 12.0 Hz), 128.62 (d, *J* = 12.9 Hz), 128.65 (d, *J* = 84.5 Hz), 131.21 (d, *J* = 2.9 Hz), 132.33 (d, *J* = 10.5 Hz), 133.58 (d, *J* = 83.1 Hz), 141.25 (d, *J* = 13.4 Hz), 145.48 (d, *J* = 10.0

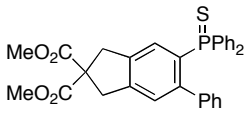
Hz), 148.64 (d, J = 2.9 Hz); ^{31}P NMR ($CDCl_3$) δ 40.83. Found: C, 77.62; H, 7.29%. Calcd for $C_{27}H_{31}PS$: C, 77.47; H, 7.46%.

(7-Hexyl-1,2,3,4,-tetrahydro-6-naphthyl)diphenylphosphine sulfide (3ea)



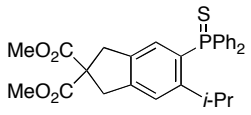
IR (neat) 3055, 2848, 2218, 1962, 1896, 1817, 1602, 1554, 1436, 1309, 1097, 1028, 912 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 7.5 Hz, 3H), 1.00–1.10 (m, 4H), 1.12–1.22 (m, 2H), 1.33–1.42 (m, 2H), 1.68–1.80 (m, 4H), 2.52 (t, J = 6.0 Hz, 2H), 2.64–2.68 (m, 2H), 2.75 (t, J = 6.0 Hz, 2H), 6.69 (d, J = 15.5 Hz, 1H), 7.04 (d, J = 5.0 Hz, 1H), 7.41–7.53 (m, 6H), 7.78–7.87 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.46, 22.84, 22.97, 28.90, 29.25, 29.26, 30.91, 31.54, 33.85 (d, J = 5.8 Hz), 128.02 (d, J = 84.5 Hz), 128.31 (d, J = 12.4 Hz), 131.19 (d, J = 2.9 Hz), 131.67 (d, J = 11.0 Hz), 132,28 (d, J = 10.5 Hz), 133.47 (d, J = 83.5 Hz), 133.77 (d, J = 12.4 Hz), 134.17 (d, J = 12.9 Hz), 141.27 (d, J = 2.9 Hz), 143.84 (d, J = 9.6 Hz); ^{31}P NMR ($CDCl_3$) δ 39.86. Found: C, 77.56; H, 7.65%. Calcd for $C_{28}H_{33}PS$: C, 77.74; H, 7.69%.

[2,2-Di(methoxycarbonyl)-6-phenyl-5-indanyl]diphenylphosphine sulfide (3cb)



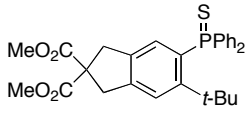
IR (nujol) 2923, 2853, 1738, 1436, 1286, 1243, 1199, 1098, 1069 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.58 (s, 2H), 3.64 (s, 2H), 3.76 (s, 6H), 6.92–7.03 (m, 3H), 7.06–7.14 (m, 3H), 7.25–7.40 (m, 7H), 7.69–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 40.36, 40.54, 53.07, 60.04, 126.91, 126.96, 128.00 (d, J = 12.5 Hz), 128.58 (d, J = 11.0 Hz), 129.31 (d, J = 12.9 Hz), 130.19, 130.86 (d, J = 2.9 Hz), 130.93 (d, J = 84.5 Hz), 132.20 (d, J = 10.0 Hz), 132.56 (d, J = 84.5 Hz), 138.85 (d, J = 13.9 Hz), 140.15 (d, J = 3.9 Hz), 143.79 (d, J = 2.9 Hz), 145.81 (d, J = 9.5 Hz), 171.73; ^{31}P NMR ($CDCl_3$) δ 40.69. Found: C, 70.48; H, 5.07%. Calcd for $C_{31}H_{27}O_4PS$: C, 70.71; H, 5.17%. m.p.: 165.0–167.0 °C.

[2,2-Di(methoxycarbonyl)-6-(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3cc)



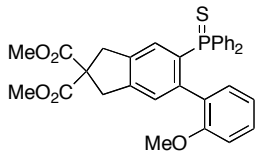
IR (nujol) 2923, 2854, 1734, 1479, 1436, 1271, 1243, 1198, 1098, 1066, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (d, *J* = 7.0 Hz, 6H), 3.43 (s, 2H), 3.57 (dsept, *J* = 1.5, 7.0 Hz, 1H), 3.61 (s, 2H), 3.74 (s, 6H), 6.67 (d, *J* = 14.5 Hz, 1H), 7.27 (d, *J* = 5.5 Hz, 1H), 7.43–7.55 (m, 6H), 7.76–7.84 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 23.66, 31.31 (d, *J* = 6.6 Hz), 40.31, 40.68, 53.02, 59.98, 124.20 (d, *J* = 11.5 Hz), 128.02 (d, *J* = 13.4 Hz), 128.40 (d, *J* = 12.0 Hz), 129.73 (d, *J* = 86.4 Hz), 131.39 (d, *J* = 2.9 Hz), 132.36 (d, *J* = 10.5 Hz), 133.18 (d, *J* = 83.5 Hz), 137.14 (d, *J* = 13.8 Hz), 144.50 (d, *J* = 2.9 Hz), 152.80 (d, *J* = 10.5 Hz), 171.84; ^{31}P NMR ($CDCl_3$) δ 40.82. Found: C, 68.08; H, 5.75%. Calcd for $C_{28}H_{29}O_4PS$: C, 68.27; H, 5.93%. m.p.: 216.0–217.5 °C.

[2,2-Di(methoxycarbonyl)-6-(1,1-dimethylethyl)-5-indanyl]diphenylphosphine sulfide (3cd)



IR (nujol) 2924, 2854, 1743, 1734, 1456, 1436, 1259, 1198, 1156, 1098, 901, 754, 707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (s, 9H), 3.37 (s, 2H), 3.63 (s, 2H), 3.74 (s, 6H), 6.86 (d, *J* = 18.0 Hz, 1H), 7.36–7.51 (m, 6H), 7.57 (d, *J* = 5.5 Hz, 1H), 7.60–7.70 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 33.51, 38.74 (d, *J* = 2.1 Hz), 40.27, 40.83, 53.03, 59.90, 126.23 (d, *J* = 12.9 Hz), 128.35 (d, *J* = 12.5 Hz), 129.18 (d, *J* = 75.9 Hz), 131.02 (d, *J* = 2.9 Hz), 132.15 (d, *J* = 13.8 Hz), 132.22 (d, *J* = 10.0 Hz), 136.51 (d, *J* = 13.9 Hz), 136.37 (d, *J* = 85.4 Hz), 144.00 (d, *J* = 2.9 Hz), 155.35 (d, *J* = 9.0 Hz), 171.86; ^{31}P NMR ($CDCl_3$) 50.66. Found: C, 68.55; H, 6.05%. Calcd for $C_{29}H_{31}O_4PS$: C, 68.76; H, 6.17%. m.p.: 165.0–166.5 °C.

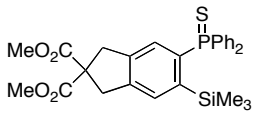
[2,2-Di(methoxycarbonyl)-6-(2-methoxyphenyl)-5-indanyl]diphenylphosphine sulfide (3ce)



IR (nujol) 2922, 2853, 1734, 1684, 1653, 1559, 1507, 1457, 1437, 1276, 1198, 1095, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.46 (s, 3H), 3.59 (s, 1H), 3.61 (s, 1H), 3.65 (s, 2H), 3.75 (s, 3H), 3.77 (s, 3H), 6.31 (d, *J* = 8.0 Hz, 1H), 6.65 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.95–7.02 (m, 1H), 7.04 (d, *J* = 4.5 Hz, 1H), 7.14–7.47 (m, 8H), 7.58–7.68 (m, 2H), 7.80–7.88 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 40.43, 40.56,

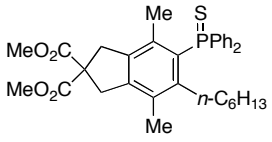
53.05, 53.09, 54.39, 59.99, 109.31, 119.00, 127.43 (d, J = 12.4 Hz), 127.90 (d, J = 12.5 Hz), 128.46 (d, J = 4.3 Hz), 128.99 (d, J = 11.9 Hz), 129.04, 129.49 (d, J = 12.9 Hz), 130.38 (d, J = 2.9 Hz), 130.83 (d, J = 2.9 Hz), 131.28 (d, J = 85.4 Hz), 131.67 (d, J = 10.5 Hz), 132.36, 132.47 (d, J = 84.5 Hz), 132.53 (d, J = 10.5 Hz), 133.65 (d, J = 84.0 Hz), 138.91 (d, J = 13.9 Hz), 141.78 (d, J = 9.6 Hz), 143.42 (d, J = 2.9 Hz), 155.69, 171.81, 171.91; ^{31}P NMR ($CDCl_3$) δ 40.56. Found: C, 68.80; H, 5.38%. Calcd for $C_{32}H_{29}O_5PS$: C, 69.05; H, 5.25%. m.p.: 89.5–92.0 ˚C.

[2,2-Di(methoxycarbonyl)-6-trimethylsilyl-5-indanyl]diphenylphosphine sulfide (3cf)



IR (nujol) 2925, 2855, 1740, 1457, 1436, 1377, 1304, 1247, 1198, 1099, 848, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9H), 3.43 (s, 2H), 3.64 (s, 2H), 3.74 (s, 6H), 6.73 (d, J = 15.0 Hz, 1H), 7.40–7.53 (m, 6H), 7.62–7.69 (m, 4H), 7.72 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 2.73, 40.59, 40.68, 53.04, 59.70, 128.37 (d, J = 12.4 Hz), 129.20 (d, J = 15.3 Hz), 131.32 (d, J = 2.9 Hz), 132.58 (d, J = 10.5 Hz), 133.84 (d, J = 17.1 Hz), 134.34 (d, J = 82.6 Hz), 137.95 (d, J = 87.8 Hz), 139.70 (d, J = 13.8 Hz), 142.33 (d, J = 2.9 Hz), 144.88 (d, J = 19.5 Hz), 171.81; ^{31}P NMR ($CDCl_3$) δ 44.97. HRMS (EI$^+$) Observed: 522.1431 (Δ = –3.6 ppm). Calcd for $C_{28}H_{31}O_4PSSi$ [M$^+$]: 522.1450. m.p.: 178.0–180.0 ˚C.

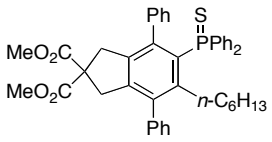
[6-Hexyl-2,2-di(methoxycarbonyl)-4,7-dimethyl-5-indanyl]diphenylphosphine sulfide (3fa)



IR (nujol) 2924, 2854, 1734, 1653, 1558, 1457, 1437, 1260, 1165, 749, 701, 651 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J = 7.5 Hz, 3H), 0.93–1.01 (m, 2H), 1.04–1.12 (m, 2H), 1.16–1.30 (m, 4H), 1.80 (s, 3H), 2.16 (s, 3H), 2.34–2.41 (m, 2H), 3.45 (s, 2H), 3.61 (s, 2H), 3.77 (s, 6H), 7.31–7.41 (m, 6H), 7.84–7.93 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.01, 15.97 (d, J = 0.9 Hz), 21.06 (d, J = 7.3 Hz), 25.51, 29.51, 30.53, 31.40, 33.04 (d, J = 7.3 Hz), 40.39 (d, J = 1.9 Hz), 40.80, 53.04, 58.67, 128.35 (d, J = 11.9 Hz), 129.73 (d, J = 88.9 Hz), 130.37 (d, J = 2.9 Hz), 130.69 (d, J = 10.5 Hz), 131.26 (d, J = 11.9 Hz), 135.63 (d, J = 11.0 Hz), 137.59 (d, J = 81.1 Hz), 138.24 (d, J = 12.9 Hz), 142.92 (d, J = 2.9

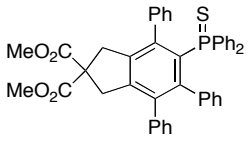
Hz), 145.76 (d, J = 10.5 Hz), 172.16; ^{31}P NMR ($CDCl_3$) δ 35.01. m.p.: 59.5–61.0 °C.

[6-Hexyl-2,2-di(methoxycarbonyl)-4,7-diphenyl-5-indanyl]diphenylphosphine sulfide (3ga)



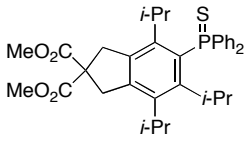
IR (nujol) 2924, 2854, 1741, 1724, 1456, 1437, 1377, 1267, 1201, 1091, 714, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.69 (t, J = 7.0 Hz, 3H), 0.72–0.86 (m, 4H), 0.95–1.05 (m, 2H), 1.16–1.27 (m, 2H), 2.46–2.54 (m, 2H), 3.26 (s, 2H), 3.37 (s, 2H), 3.66 (s, 6H), 6.90–7.04 (m, 5H), 7.10–7.23 (m, 6H), 7.24–7.46 (m, 5H), 7.56–7.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.93, 22.21, 29.17, 30.89, 30.98, 34.57 (d, J = 7.6 Hz), 40.82 (d, J = 1.3 Hz), 41.10, 52.91, 59.09, 126.71, 127.19, 127.52, 127.72 (d, J = 12.4 Hz), 128.50, 129.24, 129.73 (d, J = 2.9 Hz), 130.03 (d, J = 89.3 Hz), 130.45, 130.99 (d, J = 10.0 Hz), 136.69 (d, J = 83.1 Hz), 137.61 (d, J = 11.9 Hz), 138.91 (d, J = 4.8 Hz), 139.22 (d, J = 10.5 Hz), 139.26, 142.69 (d, J = 2.9 Hz), 143.01 (d, J = 11.0 Hz), 147.43 (d, J = 10.5 Hz), 171.90; ^{31}P NMR ($CDCl_3$) δ 36.66. Found: C, 75.23; H, 6.37%. Calcd for $C_{43}H_{43}O_4PS$: C, 75.19; H, 6.31%. m.p.: 122.0–124.0 °C.

[2,2-Di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]diphenylphosphine sulfide (3gb)



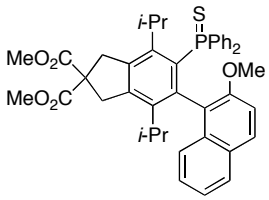
IR (nujol) 2924, 2854, 2364, 1735, 1701, 1654, 1559, 1457, 1420, 1267, 696, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 2H), 3.43 (s, 2H), 3.66 (s, 6H), 6.57–6.74 (m, 3H), 6.80–7.30 (m, 18H), 7.54–7.68 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 41.27, 41.63, 52.95, 59.00, 125.85, 126.09, 126.32, 126.72, 127.03, 127.28 (d, J = 12.4 Hz), 127.57, 129.39 (2C), 131.06, 131.11 (d, J = 85.4 Hz), 131.22 (d, J = 10.0 Hz), 133.02, 134.79 (d, J = 83.6 Hz), 137.40 (d, J = 5.1 Hz), 138.52 (d, J = 4.8 Hz), 138.86, 139.03 (d, J = 11.0 Hz), 139.92 (d, J = 11.3 Hz), 142.73 (d, J = 2.9 Hz), 143.63 (d, J = 10.5 Hz), 146.43 (d, J = 10.5 Hz), 171.81; ^{31}P NMR ($CDCl_3$) δ 36.49. Found: C, 76.06; H, 5.58%. Calcd for $C_{43}H_{35}O_4PS$: C, 76.09; H, 5.20%. m.p.: 140.0–142.0 °C.

[2,2-di(methoxycarbonyl)-4,6,7-tri(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3hc)



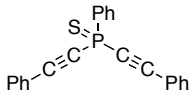
IR (neat) 2924, 2854, 1735, 1462, 1438, 1377, 1261, 1167, 1046, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75 (t, *J* = 7.0 Hz, 12H), 1.28 (d, *J* = 7.5 Hz, 6H), 3.44 (sept, *J* = 7.0 Hz, 1H), 3.47 (dsept, *J* = 2.0, 7.0 Hz, 1H), 3.54 (s, 2H), 3.68 (dsept, *J* = 2.5, 7.5 Hz, 1H), 3.69 (s, 2H), 3.76 (s, 6H), 7.26–7.36 (m, 6H), 7.82–7.93 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.72, 20.92, 22.37, 28.22, 34.22 (d, *J* = 9.1 Hz), 34.55 (d, *J* = 10.5 Hz), 39.28, 40.05, 52.92, 60.72, 128.06 (d, *J* = 11.9 Hz), 130.02 (d, *J* = 2.9 Hz), 130.57 (d, *J* = 10.0 Hz), 131.22 (d, *J* = 94.5 Hz), 137.91 (d, *J* = 12.4 Hz), 138.66 (d, *J* = 82.0 Hz), 141.96 (d, *J* = 10.5 Hz), 144.58 (d, *J* = 2.8 Hz), 147.07 (d, *J* = 11.0 Hz), 149.84 (d, *J* = 10.0 Hz), 171.86; ^{31}P NMR ($CDCl_3$) δ 35.79. Found: C, 70.55; H, 7.07%. Calcd for $C_{34}H_{41}O_4PS$: C, 70.81; H, 7.17%.

[2,2-Di(methoxycarbonyl)-6-(2-methoxy-1-naphthyl)-4,7-di(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3hg)



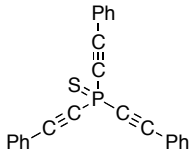
IR (nujol) 2923, 2854, 1737, 1457, 1437, 1263, 1172, 1071, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.72 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H), 1.21 (d, *J* = 7.0 Hz, 3H), 2.14 (qq, *J* = 7.0, 7.0 Hz, 1H), 3.62–3.68 (m, 2H), 3.69 (s, 3H), 3.77 (s, 3H), 3.80 (s, 3H), 3.80–3.87 (m, 2H), 4.12 (dqq, *J* = 2.5, 7.0, 7.0 Hz, 1H), 6.47 (d, *J* = 9.0 Hz, 1H), 6.72–6.81 (m, 2H), 6.87–6.90 (m, 3H), 7.14–7.40 (m, 7H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.59–7.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.93, 20.42, 20.51, 20.68, 29.72, 32.46 (d, *J* = 8.6 Hz), 40.12, 40.39, 52.97 (2C), 54.61, 60.81, 110.93, 121.68, 121.73, 123.46, 126.18 (d, *J* = 10.0 Hz), 126.28 (d, *J* = 16.8 Hz), 127.13, 127.44 (d, *J* = 10.5 Hz), 128.39, 129.06 (d, *J* = 2.9 Hz), 129.93, 130.49, 131.10 (d, *J* = 10.0 Hz), 132.02, 132.10 (d, *J* = 86.9 Hz), 134.22, 135.95 (d, *J* = 84.5 Hz), 136.92 (d, *J* = 83.0 Hz), 137.29 (d, *J* = 10.0 Hz), 140.90 (d, *J* = 12.0 Hz), 141.36 (d, *J* = 10.5 Hz), 143.15, 146.31 (d, *J* = 11.5 Hz), 153.62, 171.88, 172.04; ^{31}P NMR ($CDCl_3$) δ 40.13. m.p.: 247.5–249.0 °C.

Phenyl[di(phenylethynyl)]phosphine sulfide (5a)



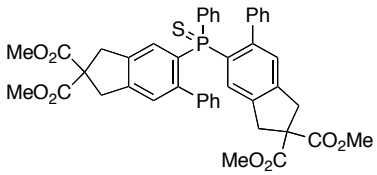
IR (nujol) 2919, 2850, 2173, 1685, 1486, 1457, 1364, 1106, 1023, 855, 766 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.34–7.47 (m, 6H), 7.54–7.63 (m, 7H), 8.18–8.26 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 82.41 (d, *J* = 176.0 Hz), 103.79 (d, *J* = 33.0 Hz), 119.93 (d, *J* = 4.8 Hz), 128.45, 128.78 (d, *J* = 15.3 Hz), 130.46 (d, *J* = 13.4 Hz), 130.67, 132.35 (d, *J* = 3.4 Hz), 132.48 (d, *J* = 2.4 Hz), 133.15 (d, *J* = 114.5 Hz); ^{31}P NMR ($CDCl_3$) δ –10.56. Found: C, 77.12; H, 4.51%. Calcd for $C_{22}H_{15}PS$: C, 77.17; H, 4.41%. m.p.: 122.0–124.0 °C.

Tri(phenylethynyl)phosphine sulfide (5b)



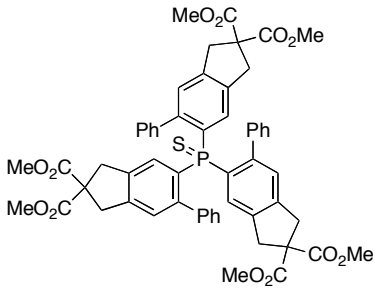
IR (nujol) 2923, 2854, 2181, 1684, 1558, 1489, 1457, 1374, 1231, 1070, 923, 852, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37–7.43 (m, 6H), 7.45–7.50 (m, 3H), 7.63–7.68 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 82.19 (d, *J* = 205.6 Hz), 102.46 (d, *J* = 40.6 Hz), 119.78 (d, *J* = 4.8 Hz), 128.53, 130.90, 132.69 (d, *J* = 2.4 Hz); ^{31}P NMR ($CDCl_3$) δ –43.59. Found: C, 78.57; H, 4.35%. Calcd for $C_{24}H_{15}PS$: C, 78.67; H, 4.13%. m.p.: 129.5–130.5 °C.

Bis[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phenylphosphine sulfide (6a)



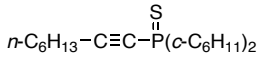
IR (nujol) 2924, 2853, 1734, 1559, 1507, 1457, 1420, 1240, 1157, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 2H), 3.54 (s, 2H), 3.61 (s, 4H), 3.79 (s, 6H), 3.81 (s, 6H), 6.85–6.91 (m, 4H), 6.92–7.01 (m, 6H), 7.08–7.14 (m, 2H), 7.20–7.26 (m, 2H), 7.31–7.46 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 40.28, 40.47, 53.05, 53.06, 60.00, 126.85, 126.92, 127.75 (d, *J* = 12.5 Hz), 128.28 (d, *J* = 10.9 Hz), 129.60 (d, *J* = 12.9 Hz), 129.79, 130.39 (d, *J* = 82.5 Hz), 130.49 (d, *J* = 2.4 Hz), 132.52 (d, *J* = 10.9 Hz), 134.47 (d, *J* = 85.4 Hz), 138.53 (d, *J* = 13.9 Hz), 140.95 (d, *J* = 3.9 Hz), 143.24 (d, *J* = 2.4 Hz), 144.79 (d, *J* = 9.5 Hz), 171.76, 171.84; ^{31}P NMR ($CDCl_3$) δ 42.93. Found: C, 69.77; H, 5.47%. Calcd for $C_{44}H_{39}O_8PS$: C, 69.64; H, 5.18%. m.p.: 124.0–126.5 °C.

Tris[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phosphine sulfide (6b)



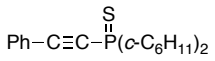
IR (nujol) 2923, 2853, 1734, 1653, 1559, 1457, 1420, 1240, 1151, 1051, 768, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.45 (s, 6H), 3.57 (s, 6H), 3.81 (s, 18H), 6.80–7.26 (m, 21H); ^{13}C NMR ($CDCl_3$) δ 40.17, 40.41, 53.02, 59.97, 126.73, 126.82, 128.17 (d, *J* = 11.0 Hz), 129.89, 130.55 (d, *J* = 81.3 Hz), 130.76 (d, *J* = 13.4 Hz), 137.82 (d, *J* = 13.9 Hz), 141.52 (d, *J* = 2.9 Hz), 142.83 (d, *J* = 2.4 Hz), 144.34 (d, *J* = 9.5 Hz), 171.84; ^{31}P NMR ($CDCl_3$) δ 44.79. Found: C, 68.75; H, 5.31%. Calcd for $C_{57}H_{51}O_{12}PS$: C, 69.08; H, 5.19%. m.p.: 157.0–160.0 °C.

Dicyclohexyl(1-octynyl)phosphine sulfide (7a)



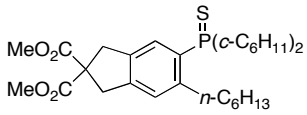
IR (neat) 2930, 2854, 2192, 1448, 1268, 1179, 1115, 1002, 887, 758, 648 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.0 Hz, 3H), 1.12–2.02 (m, 30H), 2.31 (dt, *J* = 4.0, 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.82, 19.60 (d, *J* = 2.9 Hz), 22.34, 24.83, 25.62 (d, *J* = 1.5 Hz), 26.01 (d, *J* = 15.8 Hz), 26.13 (d, *J* = 14.8 Hz), 26.20 (d, *J* = 3.4 Hz), 27.55 (d, *J* = 1.9 Hz), 28.31, 30.98, 38.49 (d, *J* = 59.3 Hz), 71.41 (d, *J* = 126.5 Hz), 107.63 (d, *J* = 18.6 Hz); ^{31}P NMR ($CDCl_3$) δ 41.71. Found: C, 70.71; H, 10.71%. Calcd for $C_{20}H_{35}PS$: C, 70.96; H, 10.42%.

Dicyclohexyl(phenylethynyl)phosphine sulfide (7b)



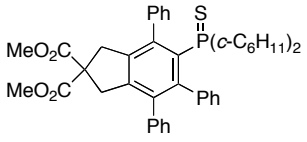
IR (nujol) 2921, 2852, 2177, 1734, 1685, 1489, 1443, 1117, 1048, 885, 757, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.12 (m, 22H), 7.33–7.38 (m, 2H), 7.39–7.44 (m, 1H), 7.50–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.05, 25.73 (d, *J* = 1.5 Hz), 26.15 (d, *J* = 14.9 Hz), 26.29 (d, *J* = 14.3 Hz), 26.47 (d, *J* = 3.9 Hz), 38.82 (d, *J* = 58.8 Hz), 80.03 (d, *J* = 120.3 Hz), 103.94 (d, *J* = 17.6 Hz), 120.52 (d, *J* = 3.3 Hz), 128.43, 130.16, 132.34 (d, *J* = 2.0 Hz); ^{31}P NMR ($CDCl_3$) δ 42.96. Found: C, 72.40; H, 8.38%. Calcd for $C_{20}H_{27}PS$: C, 72.69; H, 8.23%. m.p.: 150.0–151.5 °C.

Dicyclohexyl[6-hexyl-2,2-di(methoxycarbonyl)-5-indanyl]phosphine sulfide (8a)



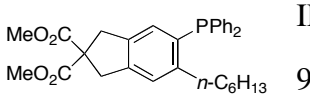
IR (neat) 2918, 2852, 2214, 1733, 1559, 1436, 1258, 1200, 1162, 1072, 913, 762, 732, 615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.0 Hz, 3H), 1.10–2.05 (m, 28H), 2.20–2.30 (m, 2H), 2.70–2.80 (m, 2H), 3.59 (s, 2H), 3.61 (s, 2H), 3.74 (s, 6H), 7.10 (d, *J* = 4.5 Hz, 1H), 8.21 (d, *J* = 15.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.61, 25.58 (d, *J* = 1.5 Hz), 26.50 (d, *J* = 11.9 Hz), 26.55 (d, *J* = 13.4 Hz), 26.56, 27.99 (d, *J* = 1.1 Hz), 29.79, 31.85, 32.13, 34.58 (d, *J* = 1.5 Hz), 39.45, 40.23 (d, *J* = 23.4 Hz), 40.47, 53.02, 60.11, 125.05, 125.57, 125.64 (d, *J* = 10.5 Hz), 131.79, 137.69 (d, *J* = 12.9 Hz), 143.53 (d, *J* = 2.4 Hz), 171.97; ^{31}P NMR ($CDCl_3$) δ 63.80.

Dicyclohexyl[2,2-di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]phosphine sulfide (8b)



IR (nujol) 2922, 2853, 1735, 1457, 1378, 1262, 1198, 1165, 1071, 771, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90–1.90 (m, 22H), 3.15 (s, 2H), 3.33 (s, 2H), 3.66 (s, 6H), 6.83–6.89 (m, 2H), 7.00–7.13 (m, 8H), 7.23–7.30 (m, 2H), 7.37–7.44 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 25.51, 26.20 (d, *J* = 13.9 Hz), 26.52 (d, *J* = 13.9 Hz), 27.06, 28.13 (d, *J* = 2.4 Hz), 40.92 (d, *J* = 48.1 Hz), 41.57, 41.84, 52.93, 58.63, 125.78 (d, *J* = 59.3 Hz), 126.19, 126.39, 127.09, 127.19, 127.55, 127.61, 129.28, 129.68, 132.07, 139.32, 139.41 (d, *J* = 2.3 Hz), 139.77 (d, *J* = 9.6 Hz), 140.69 (d, *J* = 3.3 Hz), 140.91 (d, *J* = 10.5 Hz), 141.16 (d, *J* = 2.9 Hz), 143.70, 144.30, 171.91; ^{31}P NMR ($CDCl_3$) δ 65.01. Found: C, 74.61; H, 7.15%. Calcd for $C_{43}H_{47}O_4PS$: C, 74.76; H, 6.86%. m.p.: 118.5–121.0 °C.

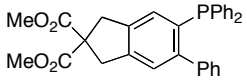
[6-Hexyl-2,2-di(methoxycarbonyl)-5-indanyl]diphenylphosphine (3ca–S)



IR (neat) 2953, 2928, 2855, 1738, 1434, 1273, 1247, 1200, 1162, 1070, 910, 734, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.5 Hz, 3H), 1.14–1.32 (m, 6H), 1.44–1.53 (m, 2H), 2.76–2.83 (m, 2H), 3.45 (s, 2H), 3.60 (s, 2H), 3.74 (s, 6H), 6.66 (d, *J* = 4.0 Hz, 1H), 7.09 (d, *J* = 4.5 Hz, 1H), 7.22–7.29 (m, 4H), 7.30–7.36 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.49, 29.23, 31.46 (d, *J* = 2.9 Hz), 31.59, 34.42 (d, *J* = 21.5 Hz), 40.34,

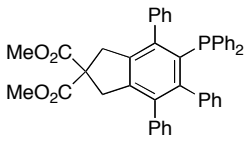
40.55, 52.92, 59.99, 124.78 (d, J = 5.8 Hz), 128.41 (d, J = 7.1 Hz), 128.48, 129.02, 133.79 (d, J = 11.0 Hz), 133.86 (d, J = 19.6 Hz), 137.23 (d, J = 11.0 Hz), 137.56, 140.98, 146.48 (d, J = 25.8 Hz), 172.16; ^{31}P NMR ($CDCl_3$) δ –16.30. Found: C, 73.73; H, 7.08%. Calcd for $C_{31}H_{35}O_4P$: C, 74.09; H, 7.02%.

[2,2-Di(methoxycarbonyl)-6-phenyl-5-indanyl]diphenylphosphine (3cb–S)



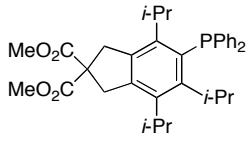
IR (nujol) 2923, 2854, 1731, 1655, 1462, 1377, 1262, 1027, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.54 (s, 2H), 3.64 (s, 2H), 3.76 (s, 6H), 6.85 (d, J = 3.5 Hz, 1H), 7.11–7.32 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 40.44, 40.53, 53.02, 59.99, 125.95 (d, J = 4.8 Hz), 127.06, 127.48, 128.32 (d, J = 6.8 Hz), 128.39, 129.47, 129.76 (d, J = 3.9 Hz), 133.89 (d, J = 19.5 Hz), 134.53 (d, J = 12.8 Hz), 137.75 (d, J = 12.5 Hz), 139.14, 140.84, 141.73 (d, J = 6.6 Hz), 147.30 (d, J = 29.0 Hz), 172.10; ^{31}P NMR ($CDCl_3$) δ –14.84. Found: C, 75.12; H, 5.55%. Calcd for $C_{31}H_{27}O_4P$: C, 75.29; H, 5.50%. m.p.: 55.5–58.0 °C.

[2,2-Di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]diphenylphosphine (3gb–S)



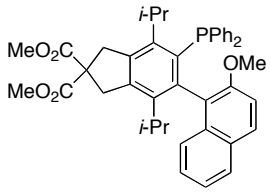
IR (nujol) 2924, 2855, 1735, 1462, 1377, 1262, 1159, 1027, 697, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.23 (s, 2H), 3.49 (s, 2H), 3.68 (s, 6H), 6.76–7.17 (m, 25H); ^{13}C NMR ($CDCl_3$) δ 41.27, 41.38, 52.88, 58.98, 125.93, 126.17 (d, J = 1.9 Hz), 126.55, 126.71, 127.49 (2C), 127.58 (d, J = 10.5 Hz), 128.68, 129.54, 130.65 (d, J = 2.4 Hz), 131.76 (d, J = 20.5 Hz), 132.12 (d, J = 19.6 Hz), 137.30, 137.41, 138.22 (d, J = 4.8 Hz), 139.58, 139.75 (d, J = 2.9 Hz), 140.11 (d, J = 3.4 Hz), 140.47, 140.56 (d, J = 7.6 Hz), 144.65 (d, J = 10.5 Hz), 148.15 (d, J = 25.3 Hz), 172.07; ^{31}P NMR ($CDCl_3$) δ –8.31. Found: C, 80.08; H, 5.71%. Calcd for $C_{43}H_{35}O_4P$: C, 79.86; H, 5.45%. m.p.: 97.5–99.5 °C.

[2,2-Di(methoxycarbonyl)-4,6,7-tri(1-methylethyl)-5-indanyl]diphenylphosphine (3hc–S)



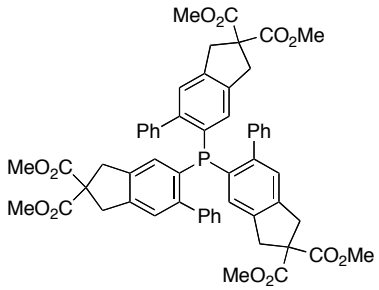
IR (neat) 2958, 2874, 2259, 1733, 1584, 1461, 1436, 1259, 1209, 1171, 1069, 910, 742, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80–1.10 (m, 12H), 1.31 (d, *J* = 7.0 Hz, 6H), 3.50–3.62 (m, 1H), 3.59 (s, 2H), 3.68 (s, 2H), 3.70–3.85 (m, 1H), 3.76 (s, 6H), 4.00–4.20 (m, 1H), 7.20–7.25 (m, 2H), 7.28–7.34 (m, 4H), 7.36–7.43 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.56, 20.80, 22.36, 28.64, 33.17 (d, *J* = 20.0 Hz), 33.93 (d, *J* = 21.6 Hz), 39.55, 40.19, 52.87, 60.83, 127.08, 128.14 (d, *J* = 4.9 Hz), 128.24 (d, *J* = 18.6 Hz), 131.39 (d, *J* = 18.1 Hz), 132.25 (d, *J* = 14.9 Hz), 137.73 (d, *J* = 16.8 Hz), 141.58, 143.40, 148.47 (d, *J* = 12.5 Hz), 151.59 (d, *J* = 10.3 Hz), 172.09; ^{31}P NMR ($CDCl_3$) δ –12.58.

[2,2-Di(methoxycarbonyl)-6-(2-methoxy-1-naphthyl)-4,7-di(1-methylethyl)-5-indanyl]diphenylphosphine (3hg–S)



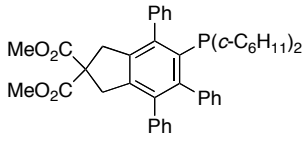
IR (nujol) 2920, 2851, 1734, 1685, 1559, 1507, 1457, 1437, 1260, 1072, 1020, 804 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.52 (d, *J* = 7.0 Hz, 3H), 0.81 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 7.0 Hz, 3H), 2.61 (qq, *J* = 7.0, 7.0 Hz, 1H), 3.17 (qq, *J* = 7.0, 7.0 Hz, 1H), 3.54 (s, 3H), 3.70 (s, 1H), 3.72 (s, 1H), 3.78 (s, 1H), 3.79 (s, 3H), 3.80 (s, 1H), 3.81 (s, 3H), 7.05–7.38 (m, 14H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.68, 20.18, 20.87, 20.89, 31.53 (d, *J* = 3.4 Hz), 32.22, 39.67, 39.84, 52.93, 52.94, 55.12, 60.72. 112.08, 123.25, 125.84, 126.51 (d, *J* = 13.9 Hz), 126.67 (d, *J* = 8.6 Hz), 127.62 (d, *J* = 11.5 Hz), 127.66 (d, *J* = 11.4 Hz), 127.88, 128.39, 128.48, 131.27 (d, *J* = 19.0 Hz), 131.77 (d, *J* = 17.6 Hz), 134.07 (d, *J* = 12.9 Hz), 134.15, 137.45 (d, *J* = 18.6 Hz), 138.53 (d, *J* = 21.0 Hz), 139.83, 140.94, 141.01, 142.11, 143.79, 144.14, 147.36 (d, *J* = 3.9 Hz), 154.21 (d, *J* = 3.8 Hz), 172.25 (2C); ^{31}P NMR ($CDCl_3$) δ –9.51. m.p.: 258.0–260.0 °C.

Tris[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phosphine (6b–S)



IR (nujol) 2924, 2854, 1731, 1655, 1462, 1377, 1239, 1158, 1049, 893, 768 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.56 (s, 6H), 3.61 (s, 6H), 3.78 (s, 18H), 6.66–6.72 (m, 6H), 6.79 (d, *J* = 2.5 Hz, 3H), 6.92 (d, *J* = 4.0 Hz, 3H), 7.01–7.08 (m, 6H), 7.10–7.15 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 40.47, 40.48, 52.99, 60.09, 125.43 (d, *J* = 4.3 Hz), 126.31, 127.01, 129.56 (d, *J* = 4.3 Hz), 130.21, 135.12 (d, *J* = 19.6 Hz), 138.75, 140.19, 141.61 (d, *J* = 6.8 Hz), 146.77 (d, *J* = 30.5 Hz), 172.18; ^{31}P NMR ($CDCl_3$) δ –27.93. m.p.: 250.0–252.0 ˚C.

Dicyclohexyl[2,2-di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]phosphine (8b–S)



IR (nujol) 2923, 2853, 2363, 1735, 1654, 1560, 1453, 1365, 1261, 1046, 952, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83–1.74 (m, 22H), 3.24 (s, 2H), 3.41 (s, 2H), 3.67 (s, 6H), 6.90–7.00 (m, 4H), 7.02–7.15 (m, 6H), 7.20–7.24 (m, 2H), 7.36–7.48 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 26.21, 26.85 (d, *J* = 17.6 Hz), 26.94 (d, *J* = 12.9 Hz), 31.59 (d, *J* = 11.5 Hz), 32.75 (d, *J* = 25.3 Hz), 35.58 (d, *J* = 15.3 Hz), 41.29, 41.41, 52.84, 59.00, 125.86, 125.93, 126.43, 126.82, 127.39, 127.85, 129.36, 129.56, 131.52, 132.32 (d, *J* = 29.1 Hz), 137.94 (d, *J* = 3.3 Hz), 138.56 (d, *J* = 3.4 Hz), 139.09, 140.06, 141.59 (2C), 144.73, 148.07, 172.17; ^{31}P NMR ($CDCl_3$) δ 0.83. m.p.: 102.0–105.0 ˚C.

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Lett. **2007**, *119*, 4925–4928. (c) Doherty, S.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Organometallics* **2008**, *28*, 4837–4840. (d) Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem., Int. Ed*. **2008**, *47*, 3410–3413.

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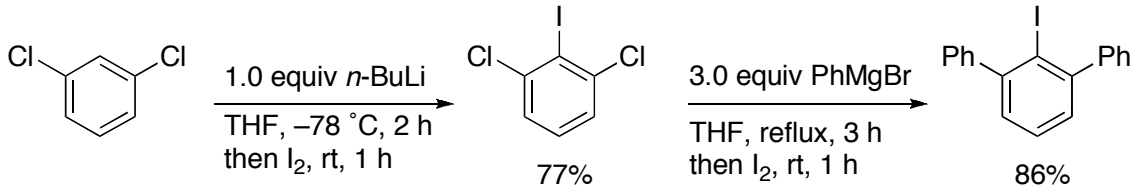
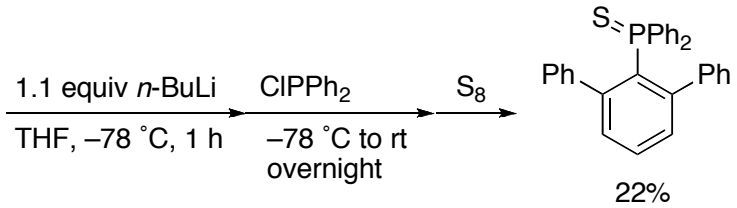
(9) The author performed the reaction of 2,6-diphenylphenyllithium with chlorodiphenylphosphine. However, the corresponding bulky phosphine, diphenyl(2,6-diphenylphenyl)phosphine, was obtained in only 22% yield, along with a significant amount of *m*-terphenyl.



Eur. J. Org. Chem. **2006**, 4398. *Tetrahedron* **1995**, *51*, 1313.



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(10) When (*R*)-Tol-BINAP was used as a ligand, a 55% ee of **3hg** was obtained in 72% yield.

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Chapter 5

New Synthesis of 2-Indolylphosphines by Palladium-Catalyzed Annulation of 1-Alkynylphosphine Sulfides with 2-Iodoanilines

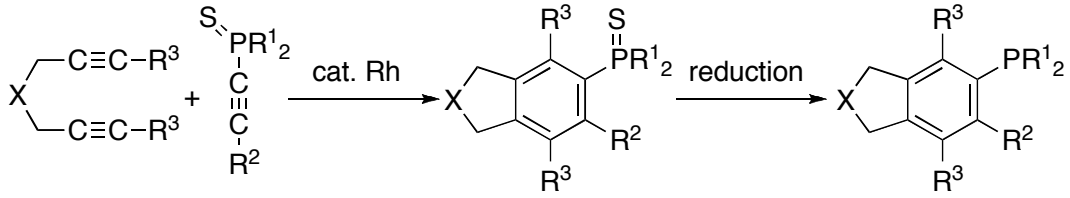
Palladium-catalyzed annulation of 1-alkynylphosphine sulfides with 2-iodoanilines followed by desulfidation affords 3-substituted 2-indolylphosphines. This annulation/desulfidation sequential protocol offers a conceptually new approach to bulky heteroarylphosphines.

Introduction

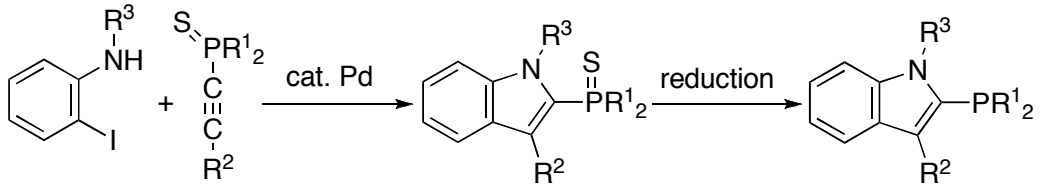
In modern organic synthesis, organophosphines play indispensable roles as ligands applicable to a broad range of transition-metal-catalyzed reactions. Creation of new phosphines and development of novel approaches to phosphines are thus quite important. Recently, bulky phosphines have attracted increasing attention as useful ligands for preparation of biologically intriguing compounds as well as functional organic materials.[1] In Chapter 4, the author disclosed a method for the synthesis of bulky arylphosphines via rhodium-catalyzed formal [2+2+2] cycloaddition reactions[2] of tethered diynes with 1-alkynylphosphine sulfides (Scheme 1).[3,4] In this reaction, the carbon–carbon triple bonds of 1-alkynylphosphine sulfides participated in the construction of benzene rings.[5]

Scheme 1. The Author's Strategies for the Synthesis of Bulky Phosphines

[2+2+2] Cycloaddition Approach (Chapter 4)



Annulation Approach (Chapter 5)



By using 1-alkynylphosphine derivatives as key starting materials, the author has developed a new strategy aiming at the synthesis of bulky heteroarylphosphines (Scheme 1). In this chapter, the author describes palladium-catalyzed annulation[6] of 1-alkynylphosphine sulfides with 2-iodoanilines to afford 2-indolylphosphine sulfides. The newly formed indole rings naturally have a substituent derived from 1-alkynylphosphine sulfides adjacent to the thiophosphinyl group, which creates a sterically congested environment around the phosphorus in cooperation with a substituent on the nitrogen atom. The product, phosphine sulfides, can be easily reduced to the

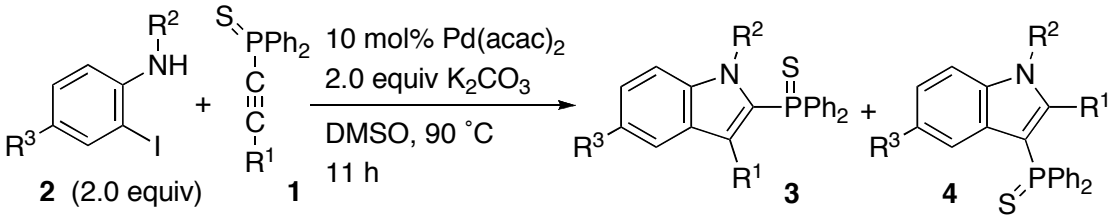
corresponding trivalent phosphines.

Although a variety of heteroarylphosphines,[7] including indole-based phosphines,[8,9] have been designed and synthesized so far, most of the syntheses involve metalation of heteroaromatic compounds followed by treating with chlorophosphines. This conventional approach requires preparation of proper heteroaromatic compounds prior to introduction of a phosphorus moiety, which sometimes necessitates a multistep synthesis. In the present reaction, incorporation of a phosphorus moiety and a substituent at the proper positions occurs at the same time as construction of a heteroaromatic ring. Hence, this protocol does not only provide new phosphines that are difficult to synthesize by other methods but also offers a conceptually new approach to heteroarylphosphines.

Results and Discussion

Annulation of 1-Alkynylphosphine Sulfides. Treatment of diphenyl(phenylethynyl)-phosphine sulfide (**1a**) with 2 equivalents of *N*-methyl-2-iodoaniline (**2a**) in the presence of a catalytic amount of bis(acetylacetonato)palladium and 2 equivalents of potassium carbonate in DMSO at 90 ˚C for 11 h afforded 2-diphenylthiophosphinyl-1-methyl-3-phenylindole (**3aa**) in 76% NMR yield and in 74% isolated yield as a major product (Table 1, entry 1).[10] Regioisomer **4aa** was also observed as a minor product (6% NMR yield), which was easily separable from **3aa** by column chromatographic purification. Choice of palladium source was important. Other palladium(II) complexes such as $Pd(OAc)_2$ and $PdCl_2$ as well as palladium(0) complexes such as $Pd_2(dba)_3$ led to lower yields. Aprotic polar solvents were suitable solvents and DMSO gave the best result. Choice of base also affected the yield. Cesium carbonate and sodium carbonate were less effective, while potassium phosphate gave a similar result to potassium carbonate. Addition of phosphine ligands such as triphenylphosphine led to lower yield. Under the reaction conditions, sulfur transfer from 1-alkynylphosphine sulfide to phosphine ligands occurred, which would deactivate the palladium catalyst.[11] The result of optimization of reaction conditions is summarized in the following section (Experimental Section, Table 2).

Table 1. Palladium-Catalyzed Annulation of 1-Alkynyldiphenylphosphine Sulfides with 2-Iodoanilines[a]



entry	1	R^1	2	R^2	R^3	3	yield /%[b]
1	**1a**	Ph	**2a**	Me	H	**3aa**	74 (6)
2	**1b**	*n*-C_6H_{13}	**2a**	Me	H	**3ba**	67 (0)
3	**1c**	*c*-C_6H_{11}	**2a**	Me	H	**3ca**	91 (0)
4	**1d**	*t*-Bu	**2a**	Me	H	**3da**	35 (0)
5	**1e**	4-Ac-C_6H_4	**2a**	Me	H	**3ea**	59 (6)
6	**1f**	4-MeO_2C-C_6H_4	**2a**	Me	H	**3fa**	58 (6)
7	**1g**	4-MeO-C_6H_4	**2a**	Me	H	**3ga**	75 (8)
8	**1h**	2-MeO-C_6H_4	**2a**	Me	H	**3ha**	54 (17)
9	**1i**	2-thienyl	**2a**	Me	H	**3ia**	57 (10)
10	**1a**	Ph	**2b**	Et	H	**3ab**	78 (6)
11	**1a**	Ph	**2c**	*i*-Pr	H	**3ac**	73 (0)
12[c]	**1a**	Ph	**2d**	Bn	H	**3ad**	59 (5)
13	**1a**	Ph	**2e**	Me	Me	**3ae**	71 (13)
14	**1a**	Ph	**2f**	Me	Cl	**3af**	56 (18)
15	**1a**	Ph	**2g**	Me	Br	**3ag**	57 (11)

[a] Conditions: **1** (0.25 mmol), **2** (0.50 mmol), $Pd(acac)_2$ (0.025 mmol), K_2CO_3 (0.50 mmol), DMSO (2.0 mL), 90 ˚C, 11 h. [b] Isolated yields of **3**. NMR yields of **4** were in parentheses. [c] The reaction was performed at 120 ˚C. Bn = $C_6H_5CH_2$.

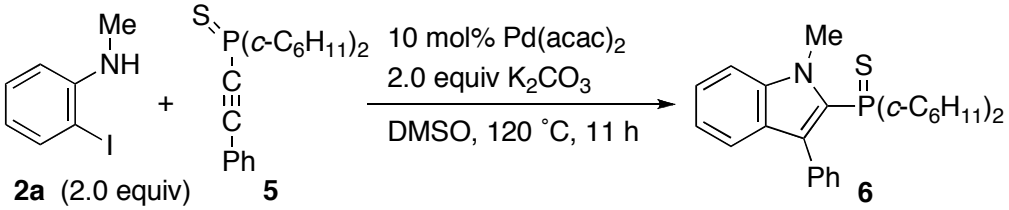
With the optimized reaction conditions in hand, the scope of 1-alkynylphosphine sulfides was investigated (Table 1, entries 1–9). Not only phenylacetylene derivative **1a** but also alkyl-substituted substrates **1b**–**1d** underwent the annulation reactions (entries 1–4). The reactions of primary and secondary-alkyl-substituted **1b** and **1c** proceeded smoothly, while *tert*-butyl-substituted **1d** provided product **3da** in low yield probably due to its bulkiness. It is worth noting that none of the regioisomers **4** were detected in the reactions of **1b**–**1d**. A variety

of functional groups, such as keto, ester, methoxy, and 2-thienyl groups, were compatible under the reaction conditions (entries 5–9).

The scope of 2-iodoaniline derivatives was examined (entries 10–15). In this reaction, an alkyl substituent on nitrogen was crucial. Primary and secondary-alkyl-substituted **2b–2d** underwent the reaction smoothly to yield the corresponding indoles in good yields. However, the reactions of *N*-acetyl-, *N*-*tert*-butoxycarbonyl-, *N*-tosyl-2-indoanilines and 2-iodoaniline did not proceed at all. Chloro and bromo groups on the benzene ring of **2** were intact under the reaction conditions. The halo moieties would allow for further transformations of **3af** and **3ag**.

1-Alkynyldicyclohexylphosphine sulfide also underwent the annulation reaction although the higher temperature was required (Scheme 2). This reaction was reliable enough to permit a gram-scale synthesis. The reaction of 1.2 g of **5** provided 1.1 g of **6** in 74% isolated yield after purification on silica gel followed by recrystallization.

Scheme 2. The Reaction of 1-Alkynyldicyclohexylphosphine Sulfide



2a (2.0 equiv) **5** **6**

0.25 mmol

3.5 mmol (1.2 g)

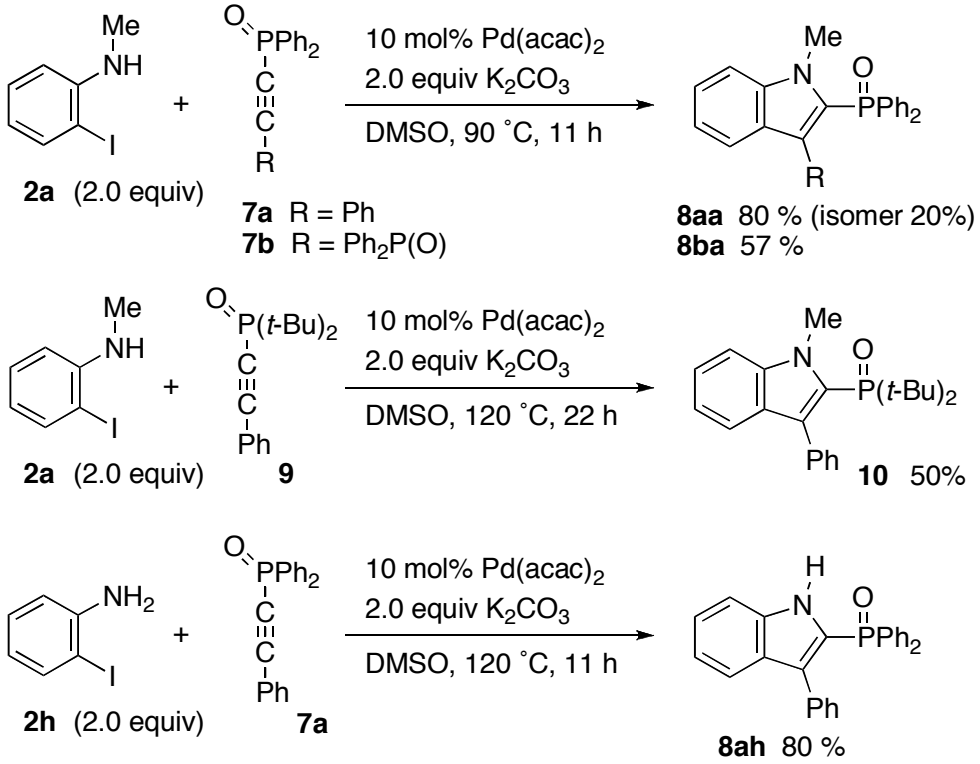
81%

74% (1.1 g)

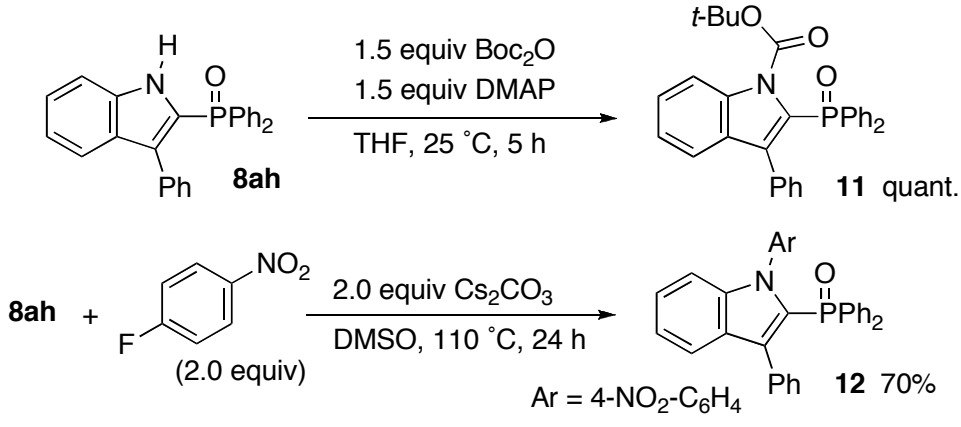
Annulation of 1-Alkynylphosphine Oxides. Next, the author tested 1-alkynylphosphine oxides instead of 1-alkynylphosphine sulfides (Scheme 3). Interestingly, the use of 1-alkynylphosphine oxides as substrates expanded the scope of accessible 2-indolylphosphines. For instance, annulation of 1,2-bis(diphenylphosphinyl)ethyne (**7b**) occurred smoothly to yield diphosphine dioxide **8ba** in good yield, while the reaction of 1,2-bis(diphenylthiophosphinyl)ethyne did not proceed. The corresponding trivalent diphosphine would serve as a bidentate ligand. 1-Alkynyl-di-*tert*-butylphosphine oxide **9** also underwent the annulation reaction in moderate yield although the longer reaction time was

required. Furthermore, 2-iodoaniline (**2h**) could react with **7a** to provide *N*-unprotected indolylphosphine oxide, which allowed for further transformations on nitrogen atom i.e. *tert*-butoxycarbonylation and arylation[12] (Scheme 4). The corresponding trivalent phosphine of **11** would serve as a potential bidentate ligand.[8c] The product **12**, which has aryl groups at the 1,3-positions, would be a potential precursor of a very bulky phosphine.

Scheme 3. The Reactions of 1-Alkynylphosphine Oxides

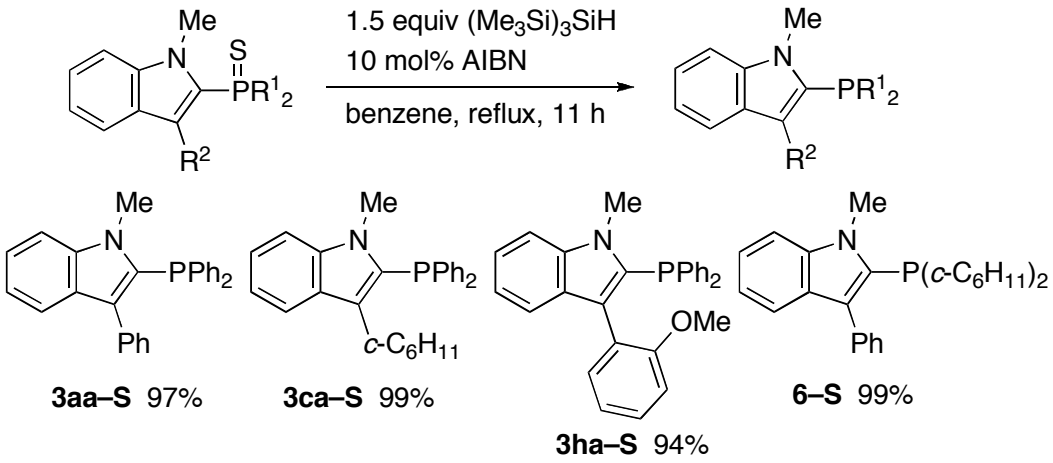


Scheme 4. Transformations of **8ah**



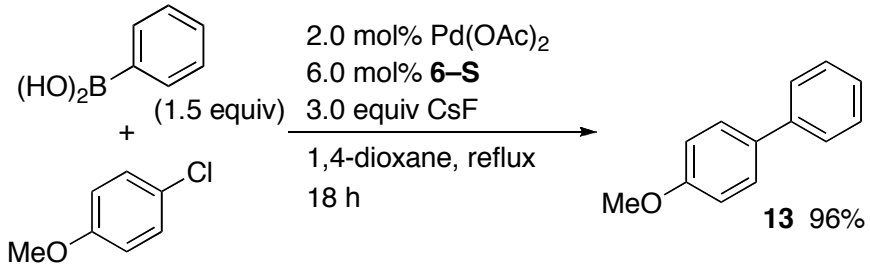
Radical Desulfidation of 2-Indolylphosphine Sulfides. Some of the phosphine sulfides thus synthesized were subjected to radical desulfidation conditions (Scheme 5).[13] Treatment of 2-indolylphosphine sulfides with tris(trimethylsilyl)silane in the presence of a catalytic amount of AIBN in benzene at reflux afforded the corresponding trivalent phosphines in good yields. The desulfidation reactions of these indolylphosphine sulfides were clean and high-yielding. The phosphines synthesized through this sequential annulation/desulfidation protocol were so stable under air that column purification on silica gel was applicable without any special care.

Scheme 5. Radical Desulfidation of 2-Indolylphosphine Sulfides



Application of Newly Synthesized 2-indolylphosphine. Finally, an application of the newly synthesized phosphine was examined. The ligand **6–S** proved to serve as an efficient ligand for Suzuki-Miyaura cross-coupling reaction of electron-rich aryl chloride (Scheme 6).[14]

Scheme 6. Suzuki-Miyaura Cross-Coupling of Aryl Chloride



Conclusion

The author has developed a conceptually new method for the synthesis of bulky indole-based heteroarylphosphines by using 1-alkynylphosphine derivatives as key starting materials. This methodology, the sequential annulation/desulfidation, offers an efficient alternative to the conventional approach to heteroarylphosphines. The phosphines synthesized by this method will find many applications in organic synthesis.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to chloroform at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.0 ppm for ^{13}C. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. NMR yields were determined by fine ^{31}P NMR spectra with $(MeO)_3P{=}O$ as an internal standard. The first delay of ^{31}P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. 1-Alkynylphosphine sulfides were prepared by using the method described in Chapter 3. *N*-Alkyl-2-iodoanilines were prepared via alkylation of 2-iodoaniline with iodoalkanes or bromoalkanes by using the method described in the literature.[15] 4-Substituted 2-iodoanilines were synthesized via iodination of 4-substituted anilines[16] followed by alkylation.

Typical Procedure for Palladium-Catalyzed Annulation reactions

$Pd(acac)_2$ (7.6 mg, 0.025 mmol) and K_2CO_3 (0.069 g, 0.50 mmol) were placed in a 20-mL reaction flask under argon. DMSO (2.0 mL), **1a** (0.080 g, 0.25 mmol), and **2a** (0.12 g, 0.50 mmol) were sequentially added. The resulting mixture was stirred at 90 ˚C for 11 h. After the mixture was cooled to room temperature, a saturated aqueous NH_4Cl (10 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Chromatographic purification on silica gel yielded **3aa**

(0.078 g, 0.18 mmol) in 74% yield as a white solid.

Procedure for *tert*-Butoxycarbonylation of 8ah (Scheme 4)

Under argon atmosphere, a mixture of **8ah** (0.039 g, 0.10 mmol), Boc_2O (0.033 g, 0.15 mmol) and DMAP (0.018 g, 0.15 mmol) in THF (2.0 mL) was stirred at ambient temperature for 5 h. Water (10 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over Na_2SO_4. Concentration followed by silica gel column purification afforded **11** (0.049 g, 0.10 mmol, quant.) as a white solid.

Procedure for Arylation of 8ah (Scheme 4)

Phosphine oxide **8ah** (0.039 g, 0.10 mmol) and Cs_2CO_3 (0.065 g, 0.20 mmol) were placed in a 20-mL reaction flask under argon. DMSO (1.0 mL) and 4-fluoronitrobenzene (0.028 g, 0.20 mmol) were sequentially added. The resulting mixture was heated at 110 ˚C for 24 h. After the mixture was cooled to room temperature, extraction with ethyl acetate (10 mL × 3) followed by silica gel column chromatography yielded **12** (0.036 g, 0.070 mmol, 70%) as a pale yellow solid.

Typical Procedure for $(Me_3Si)_3SiH$-Mediated Radical Desulfidation Reaction (Scheme 5)

Synthesis of **3aa–S** is representative. AIBN (1.6 mg, 0.010 mmol) and **3aa** (0.042 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. Benzene (2.0 mL) and tris(trimethylsilyl)silane (0.037 g, 0.15 mmol) were sequentially added. The resulting solution was stirred for 11 h at reflux. After being cooled to room temperature, the mixture was concentrated in vacuo. Silica gel column purification provided **3aa–S** (0.038 g, 0.097 mmol, 97%) as a white solid.

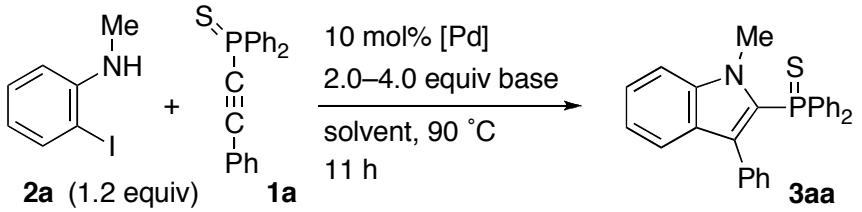
Procedure for Palladium-Catalyzed Cross-Coupling Reaction (Scheme 6)

$Pd(OAc)_2$ (2.2 mg, 0.010 mmol), **6–S** (0.012 g, 0.030 mmol), and CsF (0.23 g, 1.5 mmol)

were placed in a 20-mL reaction flask under argon. 1,4-Dioxane (2.0 mL) was added, and the mixture was stirred at room temperature for 15 min. *p*-Chloroanisole (0.071 g, 0.50 mmol) and phenylboronic acid (0.091 g, 0.75 mmol) were sequentially added, and the resulting mixture was heated at reflux for 18 h. After the mixture was cooled to room temperature, water (10 mL) was added and the product was extracted with hexane/ethyl acetate (5:1, 10 mL × 3). The combined organic layer was dried over Na_2SO_4. The crude product was purified on silica gel to provide 4-methoxybiphenyl (**13**) (0.88 g, 0.48 mmol, 96%) as a white solid.

Optimization of Reaction Conditions

Table 2. Optimization of Reaction Conditions[a]



2a (1.2 equiv) **1a** **3aa**

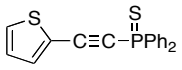
entry	[Pd]	base (equiv)	solvent	yield /%[b]
1	$Pd_2(dba)_3$[c]	K_2CO_3 (4.0)	DMF	17
2	$Pd(OAc)_2$	K_2CO_3 (4.0)	DMF	35
3	$Pd(tfa)_2$	K_2CO_3 (4.0)	DMF	12
4	$PdCl_2$	K_2CO_3 (4.0)	DMF	21
5	$PdCl_2(MeCN)_2$	K_2CO_3 (4.0)	DMF	23
6	$Pd(acac)_2$	K_2CO_3 (4.0)	DMF	46
7	$Pd(acac)_2$	K_2CO_3 (2.0)	DMF	48
8	$Pd(acac)_2$	K_2CO_3 (2.0)	DMA	39
9	$Pd(acac)_2$	K_2CO_3 (2.0)	NMP	26
10	$Pd(acac)_2$	K_2CO_3 (2.0)	DMSO	61
11	$Pd(acac)_2$	K_2CO_3 (2.0)	toluene	8
12	$Pd(acac)_2$	K_2CO_3 (2.0)	1,4-dioxane	18
13	$Pd(acac)_2$	Cs_2CO_3 (2.0)	DMSO	48
14	$Pd(acac)_2$	Na_2CO_3 (2.0)	DMSO	42
15	$Pd(acac)_2$	K_3PO_4 (2.0)	DMSO	61
16	$Pd(acac)_2$	KOAc (2.0)	DMSO	24
17[d]	$Pd(acac)_2$	K_2CO_3 (2.0)	DMSO	76

[a] Conditions: **1a** (0.25 mmol), **2a** (0.30 mmol), $Pd(acac)_2$ (0.025 mmol), base (0.50–1.0 mmol), solvent (2.0 mL), 90 ˚C, 11 h. [b] Based on ^{31}P NMR. [c] 0.013 mmol of $Pd_2(dba)_3$ was used. [d] The reaction was performed with 0.50 mmol of **2a**.

Characterization Data

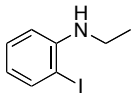
Compounds **2a**,[15] **2c**,[16] **2d**,[17] **2e**,[18] **2f**,[19] **2g**,[18] **7a**,[20] and **13**[21] showed the identical spectra as reported in the literature.

Diphenyl(2-thienylethynyl)phosphine sulfide (1i)



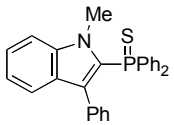
IR (nujol) 2924, 2854, 2158, 1437, 1376, 1172, 1106, 853, 717 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.03 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.44–7.56 (m, 7H), 7.93–8.03 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 85.79 (d, *J* = 150.9 Hz), 99.04 (d, *J* = 27.3 Hz), 119.80 (d, *J* = 4.8 Hz), 127.37, 128.63 (d, *J* = 13.8 Hz), 130.51, 130.83 (d, *J* = 12.0 Hz), 131.81 (d, *J* = 2.9 Hz), 133.52 (d, *J* = 98.3 Hz), 135.61 (d, *J* = 1.9 Hz); ^{31}P NMR ($CDCl_3$) δ 18.70. Found: C, 66.70; H, 3.85%. Calcd for $C_{18}H_{13}PS_2$: C, 66.64; H, 4.04%. m.p.: 86.5–88.0 °C.

***N*-Ethyl-2-iodoaniline (2b)**



IR (neat) 3391, 3066, 2968, 2872, 1590, 1507, 1450, 1317, 1164, 1004, 741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, *J* = 7.0 Hz, 3H), 3.20 (dq, *J* = 5.5, 7.0 Hz, 2H), 4.06 (br, 1H), 6.44 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.63, 38.73, 85.24, 110.50, 118.37, 129.40, 138.96, 147.36; Found: C, 38.90; H, 4.06%. Calcd for $C_8H_{10}NI$: C, 38.89; H, 4.08%.

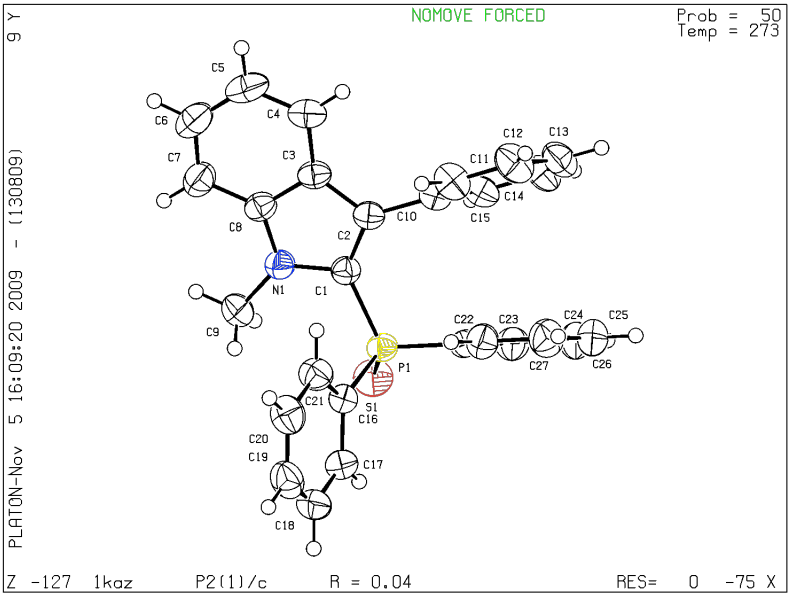
2-Diphenylthiophosphinyl-1-methyl-3-phenylindole (3aa)



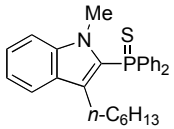
IR (nujol) 2923, 2854, 1456, 1436, 1377, 1309, 1151, 1095, 1072, 1027, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77 (s, 3H), 6.92–6.96 (m, 3H), 7.06–7.10 (m, 2H), 7.11–7.15 (m, 1H), 7.17–7.23 (m, 4H), 7.26–7.32 (m, 2H), 7.36–7.40 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.72–7.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 33.34 (d, *J* = 2.4 Hz), 109.60, 120.49, 121.13, 124.41 (d, *J* = 102.1 Hz), 124.90, 126.37, 127.49, 127.61 (d, *J* = 13.4 Hz), 127.71 (d, *J* = 12.0 Hz), 128.21 (d, *J* = 12.9 Hz), 130.86, 131.34 (d, *J* = 2.8 Hz), 131.99 (d, *J* = 10.9 Hz), 132.24 (d, *J* = 87.3 Hz), 133.30, 139.60 (d, *J* = 7.6 Hz); ^{31}P NMR ($CDCl_3$) δ 27.61. Found: C,

76.68; H, 5.33%. Calcd for $C_{27}H_{22}NPS$: C, 76.57; H, 5.24%. m.p.: 194.0–195.0 °C. CCDC No.: 753397.

Figure 1. ORTEP diagram of **3aa**

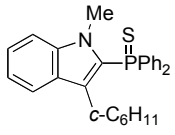


2-Diphenylthiophosphinyl-3-hexyl-1-methylindole (3ba)



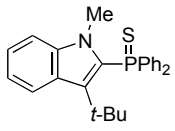
IR (nujol) 2923, 2854, 1503, 1460, 1440, 1350, 1310, 1170, 1099, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84–0.92 (m, 5H), 1.08–1.15 (m, 2H), 1.19–1.32 (m, 4H), 1.88–1.93 (m, 2H), 3.71 (s, 3H), 7.11–7.16 (m, 1H), 7.28–7.35 (m, 2H), 7.46–7.52 (m, 4H), 7.54–7.60 (m, 3H), 7.89–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.54, 24.62, 29.55, 31.56, 32.43, 33.14 (d, J = 1.9 Hz), 109.59 (d, J = 1.4 Hz), 119.52, 120.09, 123.54 (d, J = 103.5 Hz), 124.49, 127.00 (d, J = 13.9 Hz), 127.46 (d, J = 12.9 Hz), 128.64 (d, J = 12.4 Hz), 131.82 (d, J = 2.9 Hz), 132.32 (d, J = 11.5 Hz), 132.76 (d, J = 87.3 Hz), 139.93 (d, J = 8.1 Hz); ^{31}P NMR ($CDCl_3$) δ 28.20. Found: C, 75.10; H, 7.14%. Calcd for $C_{27}H_{30}NPS$: C, 75.14; H, 7.01%. m.p.: 77.0–79.0 °C.

3-Cyclohexyl-2-diphenylthiophosphinyl-1-methylindole (3ca)



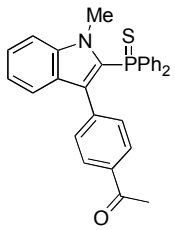
IR (nujol) 2923, 2852, 1437, 1367, 1315, 1230, 1098, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.50–0.60 (m, 2H), 1.10–1.20 (m, 1H), 1.45–1.60 (m, 5H), 1.65–1.75 (m, 1H), 1.80–1.95 (m, 2H), 3.68 (s, 3H), 7.07–7.11 (m, 1H), 7.27–7.32 (m, 2H), 7.46–7.52 (m, 4H), 7.54–7.60 (m, 2H), 7.86–7.95 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.86, 26.65, 32.29, 33.29 (d, *J* = 2.4 Hz), 35.44, 109.95 (d, *J* = 2.0 Hz), 118.99, 122.88, 123.48 (d, *J* = 104.0 Hz), 124.01, 125.87 (d, *J* = 11.9 Hz), 128.78 (d, *J* = 12.9 Hz), 131.32 (d, *J* = 13.8 Hz), 131.79 (d, *J* = 2.9 Hz), 132.05 (d, *J* = 11.0 Hz), 133.33 (d, *J* = 87.4 Hz), 140.68 (d, *J* = 8.1 Hz); ^{31}P NMR ($CDCl_3$) δ 28.44. Found: C, 75.52; H, 6.50%. Calcd for $C_{27}H_{28}NPS$: C, 75.49; H, 6.57%. m.p.: 186.5–188.0 °C.

3-*tert*-Butyl-2-diphenylthiophosphinyl-1-methylindole (3da)



IR (nujol) 2923, 2853, 1457, 1436, 1377, 1210, 1154, 1090, 751 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9H), 3.18 (s, 3H), 7.12–7.16 (m, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.28–7.32 (m, 1H), 7.35–7.44 (m, 6H), 7.94–8.02 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 32.39, 34.74, 35.37 (d, *J* = 2.9 Hz), 110.46 (d, *J* = 1.9 Hz), 119.20, 123.80 (d, *J* = 0.88 Hz), 124.11, 125.59 (d, *J* = 103.0 Hz), 127.21 (d, *J* = 12.9 Hz), 128.50 (d, *J* = 12.4 Hz), 130.87 (d, *J* = 11.0 Hz), 130.93 (d, *J* = 3.6 Hz), 137.37 (d, *J* = 85.4 Hz), 137.61 (d, *J* = 12.4 Hz), 141.81 (d, *J* = 8.6 Hz); ^{31}P NMR ($CDCl_3$) δ 30.25. Found: C, 74.52; H, 6.63%. Calcd for $C_{25}H_{26}NPS$: C, 74.41; H, 6.49%. m.p.: 143.5–145.5 °C.

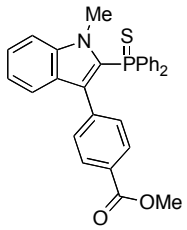
3-(4-Acetylphenyl)-2-diphenylthiophosphinyl-1-methylindole (3ea)



IR (nujol) 2924, 2854, 1736, 1682, 1607, 1457, 1437, 1356, 1265, 1245, 1096, 857 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H), 3.78 (s, 3H), 7.14–7.23 (m, 7H), 7.27–7.31 (m, 2H), 7.38–7.46 (m, 3H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.71–7.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.52, 33.40 (d, *J* = 1.6 Hz), 109.83, 120.72, 120.96, 125.14, 125.32 (d, *J* = 101.1 Hz), 126.08 (d, *J* = 11.9 Hz), 127.23 (d, *J* = 11.5 Hz),

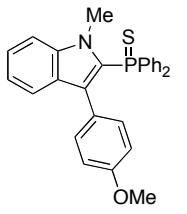
127.44, 128.33 (d, J = 12.9 Hz), 131.02, 131.40 (d, J = 3.3 Hz), 132.03 (d, J = 11.0 Hz), 132.13 (d, J = 87.4 Hz), 134.89, 138.76, 139.64 (d, J = 7.6 Hz), 197.65; ^{31}P NMR ($CDCl_3$) δ 27.46. HRMS (EI$^+$) (m/z) Observed: 465.1309 (Δ = –1.5 ppm). Calcd for $C_{29}H_{24}NOPS$ [M^+]: 465.1316. m.p.: 204.0–206.0 °C.

2-Diphenylthiophosphinyl-3-(4-methoxycarbonylphenyl)-1-methylindole (3fa)



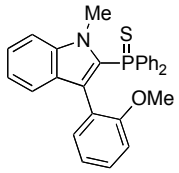
IR (nujol) 2924, 2855, 1720, 1609, 1456, 1435, 1405, 1280, 1173, 1113, 1099, 1020, 871, 832 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H), 3.91 (s, 3H), 7.12–7.17 (m, 1H), 7.14 (d, J = 8.5 Hz, 2H), 7.18–7.23 (m, 4H), 7.27–7.32 (m, 2H), 7.38–7.42 (m, 3H), 7.61 (d, J = 8.5 Hz, 2H), 7.71–7.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 33.38 (d, J = 2.4 Hz), 52.03, 109.77 (d, J = 1.5 Hz), 120.73, 120.88, 125.09, 125.19 (d, J = 101.1 Hz), 126.19 (d, J = 11.9 Hz), 127.32 (d, J = 11.4 Hz), 127.79, 128.33 (d, J = 12.9 Hz), 128.66, 130.80, 131.50 (d, J = 2.9 Hz), 131.97 (d, J = 87.3 Hz), 132.01 (d, J = 11.0 Hz), 138.53, 139.58 (d, J = 7.8 Hz), 166.93; ^{31}P NMR ($CDCl_3$) δ 27.51. Found: C, 72.53; H, 5.19%. Calcd for $C_{29}H_{24}NO_2PS$: C, 72.33; H, 5.02%. m.p.: 245.0–247.0 °C.

2-Diphenylthiophosphinyl-3-(4-methoxyphenyl)-1-methylindole (3ga)



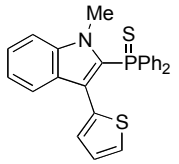
IR (nujol) 2925, 2855, 1611, 1532, 1459, 1435, 1377, 1243, 1177 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 3H), 3.75 (s, 3H), 6.47 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 7.10–7.15 (m, 1H), 7.18–7.24 (m, 4H), 7.28–7.34 (m, 2H), 7.35–7.40 (m, 2H), 7.47 (d, J = 8.0 Hz, 1H), 7.70–7.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 33.30 (d, J = 1.1 Hz), 55.19, 109.58 (d, J = 1.4 Hz), 113.17, 120.39, 121.11, 124.32 (d, J = 103.1 Hz), 124.85, 125.63, 127.33 (d, J = 12.5 Hz), 127.79 (d, J = 11.4 Hz), 128.21 (d, J = 12.9 Hz), 131.15 (d, J = 2.9 Hz), 131.90, 132.02 (d, J = 11.0 Hz), 132.42 (d, J = 88.9 Hz), 139.65 (d, J = 7.6 Hz), 158.07; ^{31}P NMR ($CDCl_3$) δ 27.55. Found: C, 74.10; H, 5.37%. Calcd for $C_{28}H_{24}NOPS$: C, 74.15; H, 5.33%. m.p.: 207.0–209.0 °C.

2-Diphenylthiophosphinyl-3-(2-methoxyphenyl)-1-methylindole (3ha)



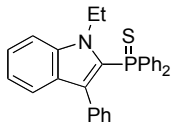
IR (nujol) 2925, 2854, 1489, 1459, 1436, 1367, 1320, 1253, 1097, 1044, 1025, 834 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 3H), 3.81 (s, 3H), 6.29 (d, *J* = 7.5 Hz, 1H), 6.70–6.75 (m, 1H), 6.91–6.97 (m, 1H), 7.06–7.16 (m, 4H), 7.20–7.30 (m, 4H), 7.32–7.38 (m, 3H), 7.58–7.64 (m, 2H), 7.84–7.90 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 33.16 (d, *J* = 1.4 Hz), 54.22, 109.52 (d, *J* = 2.1 Hz), 109.65, 119.70, 120.17, 121.14, 122.49, 122.80 (d, *J* = 12.5 Hz), 124.55, 124.73 (d, *J* = 103.5 Hz), 127.68 (d, *J* = 13.4 Hz), 127.79 (d, *J* = 13.4 Hz), 128.00 (d, *J* = 12.0 Hz), 128.55, 131.21 (d, *J* = 2.9 Hz), 131.27 (d, *J* = 88.4 Hz), 131.42 (d, *J* = 2.9 Hz), 131.87 (d, *J* = 10.9 Hz), 132.38 (d, *J* = 11.0 Hz), 132.42, 132.78 (d, *J* = 88.9 Hz), 139.68 (d, *J* = 8.0 Hz), 156.25; ^{31}P NMR ($CDCl_3$) δ 28.81. Found: C, 73.94; H, 5.51%. Calcd for $C_{28}H_{24}NOPS$: C, 74.15; H, 5.33%. m.p.: 173.5–174.0 °C.

2-Diphenylthiophosphinyl-1-methyl-3-(2-thienyl)indole (3ia)



IR (nujol) 2925, 2855, 1450, 1436, 1377, 1347, 1310, 1239, 1177, 1149, 1095, 848 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 3H), 6.50 (dd, *J* = 5.5, 4.0 Hz, 1H), 6.52 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.01 (dd, *J* = 5.5, 1.5 Hz, 1H), 7.15–7.19 (m, 1H), 7.24–7.29 (m, 4H), 7.32–7.39 (m, 4H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.76–7.82 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 33.51 (d, *J* = 1.9 Hz), 109.65 (d, *J* = 1.4 Hz), 119.34 (d, *J* = 12.0 Hz), 120.84, 121.20, 125.07, 125.81, 126.30 (d, *J* = 101.6 Hz), 127.05, 128.26 (d, *J* = 9.5 Hz), 128.28 (d, *J* = 13.0 Hz), 130.11, 131.35 (d, *J* = 3.4 Hz), 131.80 (d, *J* = 11.0 Hz), 132.27 (d, *J* = 87.9 Hz), 133.52, 139.56 (d, *J* = 7.6 Hz); ^{31}P NMR ($CDCl_3$) δ 27.55. Found: C, 69.71; H, 4.69%. Calcd for $C_{25}H_{20}NPS$: C, 69.90; H, 4.69%. m.p.: 173.0–174.0 °C.

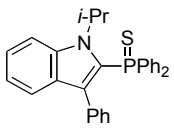
2-Diphenylthiophosphinyl-1-ethyl-3-phenylindole (3ab)



IR (nujol) 2922, 2855, 1468, 1437, 1376, 1330, 1151, 1099, 1070, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, *J* = 7.0 Hz, 3H), 4.41 (q, *J* = 7.0 Hz, 2H), 6.90–6.97 (m, 3H), 7.03–7.07 (m, 2H), 7.10–7.15 (m, 1H), 7.17–7.23 (m, 4H), 7.26–7.31 (m,

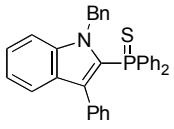
2H), 7.34–7.39 (m, 1H), 7.40–7.45 (m, 2H), 7.70–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.29, 41.37 (d, *J* = 2.9 Hz), 110.32 (d, *J* = 1.4 Hz), 120.39, 121.33, 123.95 (d, *J* = 102.6 Hz), 124.77, 126.30, 127.45, 127.50 (d, *J* = 12.4 Hz), 128.14 (d, *J* = 12.9 Hz), 128.35 (d, *J* = 11.9 Hz), 130.89, 131.32 (d, *J* = 2.9 Hz), 132.15 (d, *J* = 11.0 Hz), 132.45 (d, *J* = 87.9 Hz), 133.44, 138.54 (d, *J* = 7.6 Hz); ^{31}P NMR ($CDCl_3$) δ 27.43. Found: C, 76.68; H, 5.72%. Calcd for $C_{28}H_{24}NPS$: C, 76.86; H, 5.53%. m.p.: 165.0–166.5 ˚C.

2-Diphenylthiophosphinyl-1-isopropyl-3-phenylindole (3ac)



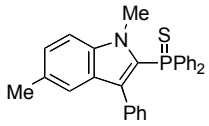
IR (nujol) 2924, 2854, 1457, 1438, 1367, 1319, 1153, 1097, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (d, *J* = 7.0 Hz, 6H), 5.39 (sept, *J* = 7.0 Hz, 1H), 6.89–6.96 (m, 3H), 6.99–7.09 (m, 3H), 7.16–7.23 (m, 4H), 7.25–7.32 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.72–7.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.39, 50.56 (d, *J* = 3.9 Hz), 112.96 (d, *J* = 0.88 Hz), 119.96, 121.60, 124.17, 124.55 (d, *J* = 102.6 Hz), 126.29, 127.08 (d, *J* = 13.4 Hz), 127.43, 128.09 (d, *J* = 12.9 Hz), 129.55 (d, *J* = 12.5 Hz), 131.00, 131.31 (d, *J* = 2.9 Hz), 132.30 (d, *J* = 11.0 Hz), 132.43 (d, *J* = 87.8 Hz), 133.51, 136.90 (d, *J* = 7.1 Hz); ^{31}P NMR ($CDCl_3$) δ 28.37. Found: C, 77.40; H, 5.69%. Calcd for $C_{29}H_{26}NPS$: C, 77.13; H, 5.80%. m.p.: 180.0–182.0 ˚C.

1-Benzyl-2-diphenylthiophosphinyl-3-phenylindole (3ad)



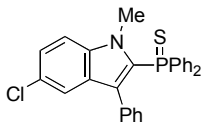
IR (nujol) 2924, 2855, 1453, 1437, 1378, 1324, 1209, 1174, 1151, 1099, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.68 (s, 2H), 6.95–7.00 (m, 5H), 7.08–7.17 (m, 11H), 7.18–7.26 (m, 3H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.68–7.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 50.06 (d, *J* = 2.4 Hz), 111.25, 120.67, 121.11, 124.74 (d, *J* = 101.1 Hz), 124.99, 126.43, 126.52, 126.80, 127.50, 128.02 (d, *J* = 13.0 Hz), 128.06, 128.11 (d, *J* = 12.4 Hz), 128.36 (d, *J* = 12.0 Hz), 130.90, 131.25 (d, *J* = 2.9 Hz), 131.95 (d, *J* = 87.9 Hz), 132.08 (d, *J* = 10.9 Hz), 133.36, 137.09, 139.43 (d, *J* = 7.6 Hz); ^{31}P NMR ($CDCl_3$) δ 27.74. Found: C, 79.27; H, 5.20%. Calcd for $C_{33}H_{26}NPS$: C, 79.33; H, 5.25%. m.p.: 159.5–160.5 ˚C.

2-Diphenylthiophosphinyl-1,5-dimethyl-3-phenylindole (3ae)



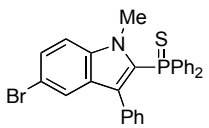
IR (nujol) 2923, 2854, 1456, 1436, 1377, 1330, 1097, 1028, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 3.75 (s, 3H), 6.92–6.97 (m, 3H), 7.05–7.09 (m, 2H), 7.16–7.24 (m, 6H), 7.25–7.31 (m, 3H), 7.70–7.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.27, 33.35, 109.35 (d, *J* = 1.4 Hz), 120.30, 124.31 (d, *J* = 102.6 Hz), 126.29, 126.77, 127.09 (d, *J* = 12.9 Hz), 127.48, 127.89 (d, *J* = 11.5 Hz), 128.18 (d, *J* = 12.9 Hz), 129.97, 130.91, 131.28 (d, *J* = 3.4 Hz), 132.02 (d, *J* = 11.5 Hz), 132.39 (d, *J* = 87.8 Hz), 133.52, 138.16 (d, *J* = 8.1 Hz); ^{31}P NMR ($CDCl_3$) δ 27.57. Found: C, 76.77; H, 5.70%. Calcd for $C_{28}H_{24}NPS$: C, 76.86; H, 5.53%. m.p.: 212.0–213.5 °C.

5-Chloro-2-diphenylthiophosphinyl-1-methyl-3-phenylindole (3af)



IR (nujol) 2924, 2854, 1457, 1437, 1376, 1331, 1270, 1098, 1058, 1028, 716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3H), 6.92–6.98 (m, 3H), 7.01–7.05 (m, 2H), 7.18–7.24 (m, 4H), 7.27–7.33 (m, 4H), 7.39 (d, *J* = 1.5 Hz, 1H), 7.70–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 33.51 (d, *J* = 2.0 Hz), 110.75 (d, *J* = 1.0 Hz), 120.30, 125.32, 126.02 (d, *J* = 100.6 Hz), 126.39, 126.65, 126.90 (d, *J* = 12.4 Hz), 127.66, 128.30 (d, *J* = 12.9 Hz), 128.69 (d, *J* = 11.5 Hz), 130.76, 131.49 (d, *J* = 2.9 Hz), 131.96 (d, *J* = 87.9 Hz), 131.99 (d, *J* = 11.0 Hz), 132.69, 137.95 (d, *J* = 7.6 Hz); ^{31}P NMR ($CDCl_3$) δ 27.63. Found: C, 70.57; H, 4.47%. Calcd for $C_{27}H_{21}ClNPS$: C, 70.81; H, 4.62%. m.p.: 175.5–177.0 °C.

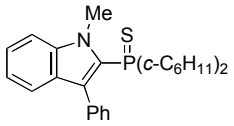
5-Bromo-2-diphenylthiophosphinyl-1-methyl-3-phenylindole (3ag)



IR (nujol) 2924, 2854, 1479, 1436, 1377, 1270, 1100, 1071, 1028, 874 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3H), 6.92–6.98 (m, 3H), 7.01–7.06 (m, 2H), 7.18–7.26 (m, 5H), 7.27–7.32 (m, 2H), 7.41–7.45 (m, 1H), 7.54 (d, *J* = 1.5 Hz, 1H), 7.69–7.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 33.48, 111.14, 113.82 (d, *J* = 1.4 Hz), 123.43, 125.89 (d, *J* = 100.8 Hz), 126.66, 126.80 (d, *J* = 12.4 Hz), 127.67, 127.82, 128.30 (d, *J* = 12.9 Hz), 129.32 (d, *J* = 11.5 Hz), 130.76, 131.49 (d, *J* = 3.4 Hz), 131.92 (d, *J* = 87.3 Hz), 131.98 (d, *J*

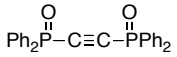
= 11.0 Hz), 132.63, 138.19 (d, J = 7.6 Hz); ^{31}P NMR ($CDCl_3$) δ 27.59. HRMS (EI^+) (*m/z*) Observed: 501.0313 (Δ = –0.6 ppm). Calcd for $C_{27}H_{21}NPSBr$ [M^+]: 501.0316. m.p.: 198.0–200.0 ˚C.

2-Dicyclohexylthiophosphinyl-1-methyl-3-phenylindole (6)



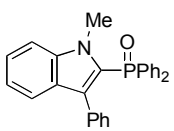
IR (nujol) 2923, 2853, 1448, 1374, 1320, 1206, 1004, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87–1.20 (m, 6H), 1.46–1.72 (m, 10H), 1.73–1.96 (m, 6H), 4.41 (s, 3H), 7.08 (dd, J = 7.5, 7.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.31–7.38 (m, 3H), 7.41 (d, J = 8.5 Hz, 1H), 7.45–7.52 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 25.56 (d, J = 1.5 Hz), 26.06 (d, J = 13.9 Hz), 26.21 (d, J = 2.4 Hz), 26.37 (d, J = 14.3 Hz), 26.96 (d, J = 2.9 Hz), 34.47, 39.89 (d, J = 51.5 Hz), 109.70, 120.37, 120.52, 121.86 (d, J = 74.0 Hz), 124.28, 124.54 (d, J = 11.5 Hz), 127.76, 128.29, 128.40 (d, J = 11.0 Hz), 130.89, 135.38, 139.77 (d, J = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ 52.51. Found: C, 74.44; H, 7.96%. Calcd for $C_{27}H_{34}NPS$: C, 74.45; H, 7.87%. m.p.: 154.0–155.0 ˚C.

1,2-Bis(diphenylphosphinyl)ethyne (7b)



IR (nujol) 2924, 2855, 1442, 1377, 1328, 1207, 1122, 1103, 1074, 993, 800, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.44–7.51 (m, 8H), 7.54–7.60 (m, 4H), 7.76–7.84 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 99.00 (dd, J = 136.0, 17.1 Hz), 128.89 (m), 130.96 (d, J = 121.8 Hz), 131.05 (m), 132.96; ^{31}P NMR ($CDCl_3$) δ 7.30. Found: C, 73.19; H, 4.80%. Calcd for $C_{26}H_{20}O_2P_2$: C, 73.24; H, 4.73%. m.p.: 154.0–156.0 ˚C.

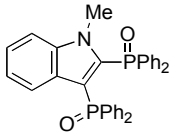
2-Diphenylphosphinyl-1-methyl-3-phenylindole (8aa)



IR (nujol) 2923, 2853, 1456, 1437, 1323, 1183, 1103, 840, 702, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.93 (s, 3H), 6.89–6.70 (m, 5H), 7.09–7.14 (m, 1H), 7.19–7.25 (m, 4H), 7.32–7.43 (m, 5H), 7.47–7.54 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 32.91, 109.59, 120.32, 121.26, 125.00, 125.27 (d, J = 118.9 Hz), 126.32, 127.40, 127.96 (d, J = 11.5 Hz),

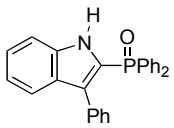
128.26 (d, *J* = 12.5 Hz), 128.40 (d, *J* = 14.8 Hz), 130.68, 131.69 (d, *J* = 2.9 Hz), 131.83 (d, *J* = 10.0 Hz), 132.68 (d, *J* = 108.9 Hz), 133.38, 139.25 (d, *J* = 8.1 Hz); ^{31}P NMR ($CDCl_3$) δ 19.06. HRMS (EI^+) (*m/z*) Observed: 407.1438 (Δ = –0.3 ppm). Calcd for $C_{27}H_{22}NOP$ [M^+]: 407.1439. m.p.: 173.5–174.5 °C.

2,3-Bis(diphenylphosphinyl)-1-methylindole (8ba)



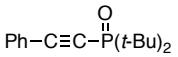
IR (nujol) 2924, 2855, 2360, 2323, 1456, 1436, 1181, 1119, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.21 (s, 3H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.17–7.30 (m, 13H), 7.32–7.46 (m, 5H), 7.82–7.92 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 34.23, 110.51, 112.76 (dd, *J* = 119.4, 13.4 Hz), 121.66, 121.81, 124.25, 127.63 (d, *J* = 13.4 Hz), 128.18 (d, *J* = 12.4 Hz), 128.95 (dd, *J* = 11.0, 10.0 Hz), 131.32 (d, *J* = 2.4 Hz), 131.41 (d, *J* = 10.5 Hz), 131.78 (d, *J* = 2.9 Hz), 132.62 (d, *J* = 112.6 Hz), 132.80 (d, *J* = 11.0 Hz), 134.68 (d, *J* = 107.9 Hz), 138.72 (dd, *J* = 106.4, 17.6 Hz), 140.45 (dd, *J* = 10.6, 8.1 Hz); ^{31}P NMR ($CDCl_3$) δ 20.41, 26.08. HRMS (EI^+) (*m/z*) Observed: 531.1525 (Δ = +1.5 ppm). Calcd for $C_{33}H_{27}NO_2P_2$ [M^+]: 531.1517. m.p.: 200.0–202.0 °C.

2-Diphenylphosphinyl-3-phenylindole (8ah)



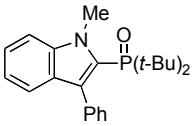
IR (nujol) 2923, 2854, 1456, 1439, 1377, 1162, 1121, 828, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.06–7.17 (m, 6H), 7.28–7.37 (m, 5H), 7.42–7.50 (m, 3H), 7.51–7.62 (m, 5H), 9.56 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 111.90, 120.68, 120.80, 124.17 (d, *J* = 119.9 Hz), 124.76, 126.68 (d, *J* = 12.9 Hz), 126.82, 127.84, 128.34 (d, *J* = 12.9 Hz), 128.63 (d, *J* = 11.5 Hz), 130.45, 131.94 (d, *J* = 10.5 Hz), 131.99 (d, *J* = 109.3 Hz), 132.05 (d, *J* = 2.9 Hz), 133.37, 137.18 (d, *J* = 10.0 Hz); ^{31}P NMR ($CDCl_3$) δ 19.76. Found: C, 78.99; H, 5.12%. Calcd for $C_{26}H_{20}NOP$: C, 79.38; H, 5.12%. m.p.: 208.0–210.0 °C.

Di-*tert*-butyl(phenylethynyl)phosphine oxide (9)



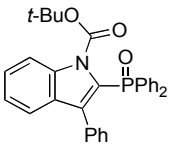
IR (nujol) 2923, 2854, 2181, 1490, 1448, 1363, 1155, 837, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (d, *J* = 15.0 Hz, 18H), 7.37 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.55 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.42, 36.24 (d, *J* = 72.0 Hz), 81.75 (d, *J* = 126.9 Hz), 103.00 (d, *J* = 18.6 Hz), 120.64 (d, *J* = 3.4 Hz), 128.52, 130.11, 132.30 (d, *J* = 1.5 Hz); ^{31}P NMR ($CDCl_3$) δ 46.41. Found: C, 73.02; H, 8.89%. Calcd for $C_{16}H_{23}OP$: C, 73.26; H, 8.84%. m.p.: 124.0–126.0 °C.

2-Di-*tert*-butylphosphinyl-1-methyl-3-phenylindole (10)



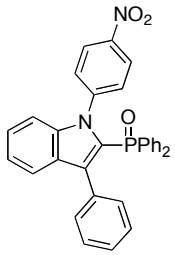
IR (nujol) 2923, 2854, 1684, 1447, 1363, 1307, 1201, 1155, 825, 818 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (d, *J* = 14.5 Hz, 18H), 4.40 (s, 3H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.33 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.39–7.42 (m, 5H), 7.44 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.91 (d, *J* = 0.90 Hz), 34.01, 37.50 (d, *J* = 61.0 Hz), 109.68, 120.01, 120.85, 123.85 (d, *J* = 12.9 Hz), 123.94, 124.22 (d, *J* = 78.8 Hz), 127.72, 127.78, 129.86 (d, *J* = 10.5 Hz), 132.50, 136.06, 139.27 (d, *J* = 6.6 Hz); ^{31}P NMR ($CDCl_3$) δ 60.10. HRMS (EI^+) (*m/z*) Observed: 367.2068 (Δ = +0.8 ppm). Calcd for $C_{23}H_{30}NOP$ [M^+]: 367.2065. m.p.: 112.5–114.0 °C.

1-*tert*-Butoxycarbonyl-2-diphenylphosphinyl-3-phenylindole (11)



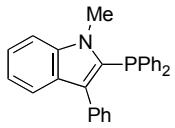
IR (nujol) 2921, 2852, 1731, 1701, 1438, 1317, 1300, 1149 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9H), 7.00–7.30 (m, 12H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.47 (dd, *J* = 7.5, 7.0 Hz, 1H), 7.50–7.63 (m, 4H), 8.19 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.51, 85.64, 115.25, 121.23, 123.26, 126.67 (d, *J* = 117.0 Hz), 127.43, 127.64, 127.91 (d, *J* = 12.4 Hz), 127.92, 129.51 (d, *J* = 11.5 Hz), 130.68 (d, *J* = 2.9 Hz), 130.86, 131.02 (d, *J* = 10.0 Hz), 132.48 (d, *J* = 1.5 Hz), 135.08 (d, *J* = 111.6 Hz), 137.69 (d, *J* = 12.9 Hz), 137.89 (d, *J* = 5.8 Hz), 149.82; ^{31}P NMR ($CDCl_3$) δ 14.76. HRMS (EI^+) (*m/z*) Observed: 493.1797 (Δ = –2.0 ppm). Calcd for $C_{31}H_{28}NO_3P$ [M^+]: 493.1807. m.p.: 61.0–63.0 °C.

2-Diphenylphosphinyl-1-(4-nitrophenyl)-3-phenylindole (12)



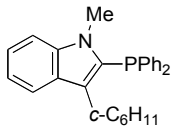
IR (nujol) 2922, 2853, 1593, 1510, 1497, 1440, 1346, 1203, 1189, 1099, 871, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.02–7.10 (m, 7H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.17–7.25 (m, 3H), 7.28–7.37 (m, 3H), 7.43–7.50 (m, 4H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 110.45, 121.64, 122.01, 123.95, 126.32, 127.27, 127.68 (d, *J* = 10.9 Hz), 127.89, 127.95 (d, *J* = 115.4 Hz), 127.97 (d, *J* = 12.4 Hz), 129.87, 130.78, 131.27 (d, *J* = 2.9 Hz), 131.37 (d, *J* = 9.5 Hz), 132.24 (d, *J* = 12.9 Hz), 132.51 (d, *J* = 108.8 Hz), 132.69, 139.76 (d, *J* = 7.3 Hz), 143.77, 146.44; ^{31}P NMR ($CDCl_3$) δ 12.70. HRMS (EI^+) (*m*/*z*) Observed: 514.1452 (Δ = +1.1 ppm). Calcd for $C_{32}H_{23}N_2O_3P$ [M^+]: 514.1446. m.p.: 236.0–237.0 °C.

2-Diphenylphosphino-1-methyl-3-phenylindole (3aa–S)



IR (nujol) 2923, 2853, 1507, 1457, 1430, 1369, 1340, 1324, 1275, 1261, 1149, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.33 (s, 3H), 7.17–7.22 (m, 1H), 7.28–7.36 (m, 9H), 7.37–7.43 (m, 6H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.49 (d, *J* = 2.9 Hz), 109.46, 119.92, 120.49 (d, *J* = 1.9 Hz), 123.72, 126.68, 127.31 (d, *J* = 8.0 Hz), 127.86, 128.01, 128.57 (d, *J* = 5.8 Hz), 129.04 (d, *J* = 28.6 Hz), 131.05 (d, *J* = 31.0 Hz), 131.06 (d, *J* = 3.4 Hz), 131.69 (d, *J* = 17.6 Hz), 134.93 (d, *J* = 3.9 Hz), 135.73 (d, *J* = 11.4 Hz), 139.66; ^{31}P NMR ($CDCl_3$) δ –32.15. Found: C, 82.77; H, 5.72%. Calcd for $C_{27}H_{22}NP$: C, 82.84; H, 5.66%. m.p.: 159.5–160.5 °C.

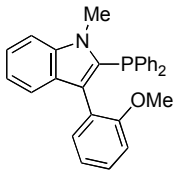
3-Cyclohexyl-2-diphenylphosphino-1-methylindole (3ca–S)



IR (nujol) 2922, 2851, 1583, 1505, 1479, 1447, 1373, 1320, 1189, 1136, 1091, 1016, 887 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25–1.42 (m, 3H), 1.72–1.84 (m, 5H), 2.04–2.14 (m, 2H), 3.28–3.36 (m, 1H), 3.60 (s, 3H), 7.11–7.15 (m, 1H), 7.26–7.39 (m, 8H), 7.40–7.45 (m, 4H), 7.95 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.32, 27.13, 32.13 (d, *J* = 6.6 Hz), 33.56, 37.85 (d, *J* = 14.4 Hz), 109.66, 118.46, 121.55, 122.86, 126.19 (d, *J* = 7.1

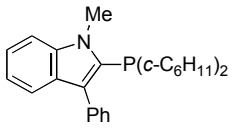
Hz), 127.65 (d, *J* = 19.5 Hz), 127.92, 128.53 (d, *J* = 5.8 Hz), 131.63 (d, *J* = 17.8 Hz), 134.25 (d, *J* = 23.4 Hz), 135.83 (d, *J* = 9.6 Hz), 140.15 (d, *J* = 1.4 Hz); ^{31}P NMR ($CDCl_3$) δ –36.05. HRMS (EI$^+$) (*m/z*) Observed: 397.1956 (Δ = –0.9 ppm). Calcd for $C_{27}H_{28}NP$ [M$^+$]: 397.1959. m.p.: 133.0–135.0 ˚C.

2-Diphenylphosphino-3-(2-methoxyphenyl)-1-methylindole (3ha–S)



IR (nujol) 2922, 2853, 1457, 1369, 1322, 1240, 1081, 941, 801 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 3H), 3.42 (s, 3H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.10–7.16 (m, 1H), 7.20–7.40 (m, 12H), 7.42–7.48 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.39 (d, *J* = 3.4 Hz), 54.59, 109.33, 110.59, 119.58, 120.02, 120.60 (d, *J* = 1.4 Hz), 123.24, 124.01 (d, *J* = 4.4 Hz), 126.04 (d, *J* = 32.5 Hz), 127.78, 127.80, 127.81 (d, *J* = 3.6 Hz), 128.30 (d, *J* = 5.3 Hz), 128.32, 128.39 (d, *J* = 5.8 Hz), 130.25 (d, *J* = 26.3 Hz), 131.74 (d, *J* = 17.8 Hz), 131.99 (d, *J* = 17.1 Hz), 132.73, 135.69 (d, *J* = 11.0 Hz), 136.20 (d, *J* = 11.0 Hz), 139.70, 157.55; ^{31}P NMR ($CDCl_3$) δ –29.98. HRMS (EI$^+$) (*m/z*) Observed: 421.1600 (Δ = +1.1 ppm). Calcd for $C_{28}H_{24}NOP$ [M$^+$]: 421.1596. m.p.: 63.0–65.0 ˚C.

2-Dicyclohexylphosphino-1-methyl-3-phenylindole (6–S)



IR (nujol) 2924, 2851, 1456, 1441, 1389, 1320, 1243, 1151, 1031, 771 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96–2.06 (m, 22H), 3.98 (s, 3H), 7.10 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.26–7.31 (m, 1H), 7.35–7.48 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 26.17, 26.85 (d, *J* = 13.9 Hz), 26.86 (d, *J* = 10.5 Hz), 30.76 (d, *J* = 8.6 Hz), 31.99 (d, *J* = 13.9 Hz), 32.65 (d, *J* = 22.9 Hz), 35.40 (d, *J* = 8.6 Hz), 109.21, 119.46, 119.68, 122.55, 126.61, 127.80, 128.42, 131.07, 131.57, 131.75, 136.11, 138.67; ^{31}P NMR ($CDCl_3$) δ –21.53. HRMS (EI$^+$) (*m/z*) Observed: 403.2426 (Δ = –0.8 ppm). Calcd for $C_{27}H_{34}NP$ [M$^+$]: 403.2429. m.p.: 89.0–91.0 ˚C.

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Chapter 6

Rhodium-Catalyzed Reaction of 1-Alkynylphosphines with Water Yielding (*E*)-1-Alkenylphosphine Oxides

Treatment of 1-alkynylphophines with a rhodium catalyst in 1,4-dioxane/H_2O at reflux provides (*E*)-1-alkenylphosphine oxides in good yields with perfect stereoselectivity.

Introduction

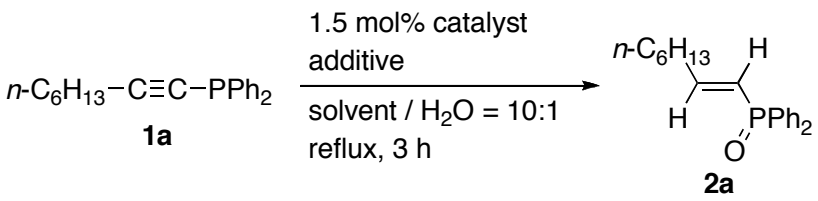
During the course of his study on the use of 1-alkynylphosphine derivatives as key starting materials for the synthesis of new phosphines, the author found a new transformation of 1-alkynylphosphines. 1-Alkynylphosphines react with water in the presence of a rhodium catalyst to provide the corresponding (*E*)-1-alkenylphosphine oxides[1] with perfect stereoselectivity. This is an interesting formal hydration reaction of 1-alkynylphosphines from mechanistic and synthetic points of view.

Results and Discussion

Treatment of 1-octynyldiphenylphosphine (**1a**) under $[RhCl(cod)]_2$ catalysis in 1,4-dioxane/H_2O (10:1) at reflux provided (*E*)-1-octenyldiphenylphosphine oxide (**2a**) in 84% NMR yield and 73% isolated yield (Table 1, entry 1). Other rhodium complexes such as $[Rh(OH)(cod)]_2$ also showed catalytic activity (entry 2). Addition of PPh_3 (2 equiv to Rh) as a ligand had no effect on the reactivity (entry 3). In contrast, when BINAP (1 equiv to Rh) or $P(OEt)_3$ (2 equiv to Rh) was used instead of PPh_3, the reaction was completely inhibited (entries 4 and 5). $Rh(acac)_3$ and an iridium catalyst, $[IrCl(cod)]_2$, were inactive (entries 6 and 7).

1,4-Dioxane/H_2O was the choice of solvent. Although the reaction proceeded in a toluene/H_2O mixed solvent, the reaction suffered from poor reproducibility (entry 8). When toluene was used, the reaction proceeded in a two-phase medium. The erratic amount of water in the nonpolar organic phase would be responsible for the poor reproducibility. When THF or acetonitrile was used instead of 1,4-dioxane, the reaction did not proceed, albeit the reaction is homogeneous (entries 9 and 10). The reaction in a 1,2-dichloroethane/H_2O biphasic medium failed, probably because of the highly hydrophobic nature of 1,2-dichloroethane (entry 11). The use of 1,4-dioxane without H_2O resulted in complete recovery of **1a** (entry 12). When the amount of water was reduced to 3 equivalents to the alkynylphosphine, poor reproducibility was observed (entry 13). The amount of water in the organic phase is the key for reproducibility.

Table 1. Optimization of Reaction Conditions[a]

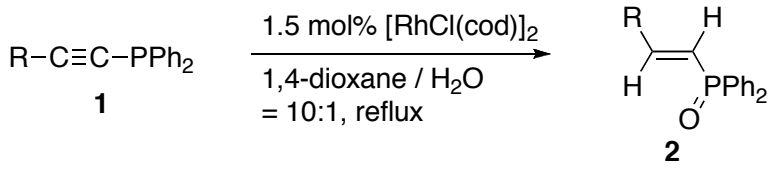


entry	catalyst	additive	solvent[b]	yield /%[c]
1	$[RhCl(cod)]_2$	none	1,4-dioxane	84 (73)
2	$[Rh(OH)(cod)]_2$	none	1,4-dioxane	75
3	$[RhCl(cod)]_2$	PPh_3[d]	1,4-dioxane	85
4	$[RhCl(cod)]_2$	BINAP[e]	1,4-dioxane	0
5	$[RhCl(cod)]_2$	$P(OEt)_3$[d]	1,4-dioxane	0
6	$Rh(acac)_3$	none	1,4-dioxane	0
7	$[IrCl(cod)]_2$	none	1,4-dioxane	0
8	$[RhCl(cod)]_2$	none	toluene[f]	0–84
9	$[RhCl(cod)]_2$	none	THF	0
10	$[RhCl(cod)]_2$	none	acetonitrile	0
11	$[RhCl(cod)]_2$	none	1,2-dichloroethane[f]	0
12[g]	$[RhCl(cod)]_2$	none	1,4-dioxane	0
13[h]	$[RhCl(cod)]_2$	none	1,4-dioxane	0–84

[a] Conditions: **1a** (0.50 mmol), $[RhCl(cod)]_2$ (0.0075 mmol), 1,4-dioxane (3.0 mL), H_2O (0.30 mL), reflux, 3 h. [b] The reaction is homogeneous unless otherwise noted. [c] Based on ^{31}P NMR with a sufficient first decay period. Isolated yield is in parenthesis. [d] 2 equiv to Rh. [e] 1 equiv to Rh. [f] The reaction proceeded in a two-phase medium. [g] The reaction was performed without H_2O. [h] The reaction was performed with H_2O (3 equiv to **1a**).

The scope of 1-alkynylphosphines was investigated (Table 2). Although a bulky *tert*-butyl group of **1d** completely suppressed the reaction,[2] phenyl- and isopropyl-substituted alkynylphosphines **1b** and **1c** underwent the reaction. The reactions of methoxyphenyl-substituted **1e** and **1f** and *p*-acetylphenyl-substituted **1g** proceeded smoothly. However, neither pyridine-containing **1h**, hydroxy group-containing **1i**, nor 1-octynyldicyclohexylphosphine reacted.

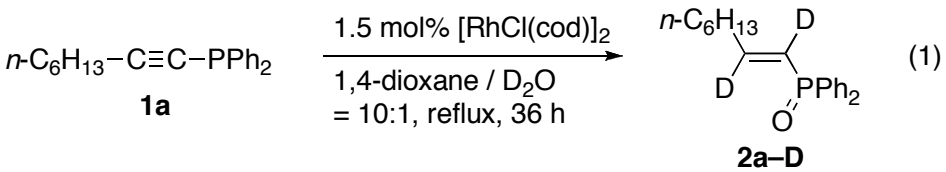
Table 2. Synthesis of (*E*)-1-Alkenylphosphine Oxides[a]



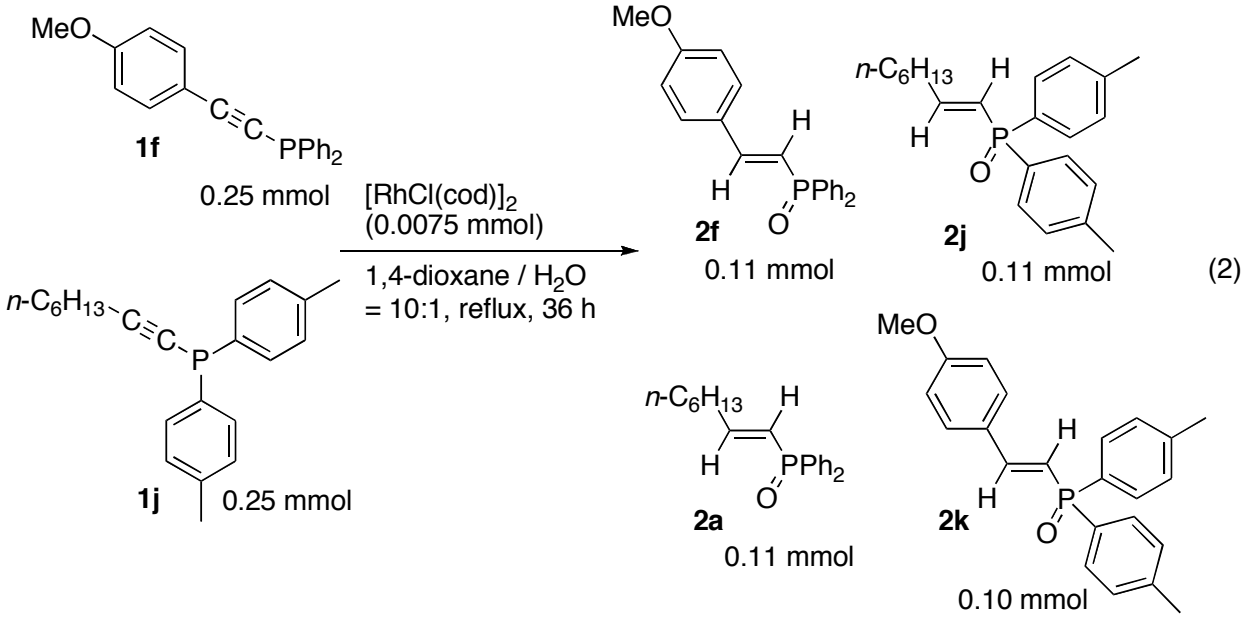
entry	R	time /h	yield /%[b]
1	Ph (**1b**)	6	72
2	*i*-Pr (**1c**)	8	69
3	*t*-Bu (**1d**)	8	0
4	2-MeO-C_6H_4 (**1e**)	21	72
5	4-MeO-C_6H_4 (**1f**)	7	75
6	4-Ac-C_6H_4 (**1g**)	5	62
7	2-pyridyl (**1h**)	12	0
8	PhCH(OH) (**1i**)	12	0

[a] Conditions: **1** (0.50 mmol), $[RhCl(cod)]_2$ (0.0075 mmol), 1,4-dioxane (3.0 mL), H_2O (0.30 mL). [b] Isolated yields.

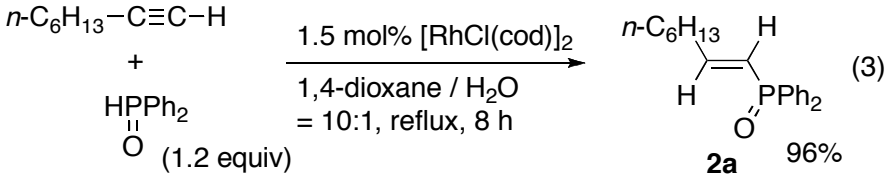
Reaction Mechanism. To reveal the mechanism of this reaction, the author carried out the following two experiments. First, D_2O was used instead of H_2O. As a result, the product deuterated at the two alkenylpositions was obtained as the sole product (eq 1). From a mechanistic point of view, it is worth noting that the reaction in 1,4-dioxane/D_2O was slow (vide infra). Next, a mixture of **1f** and **1j** was exposed to the reaction conditions. In this case, four 1-alkenylphosphine oxides were obtained in almost equal amounts (eq 2). This result suggests that cleavage of the C_{sp}–P bonds of 1-alkynylphosphines would occur.



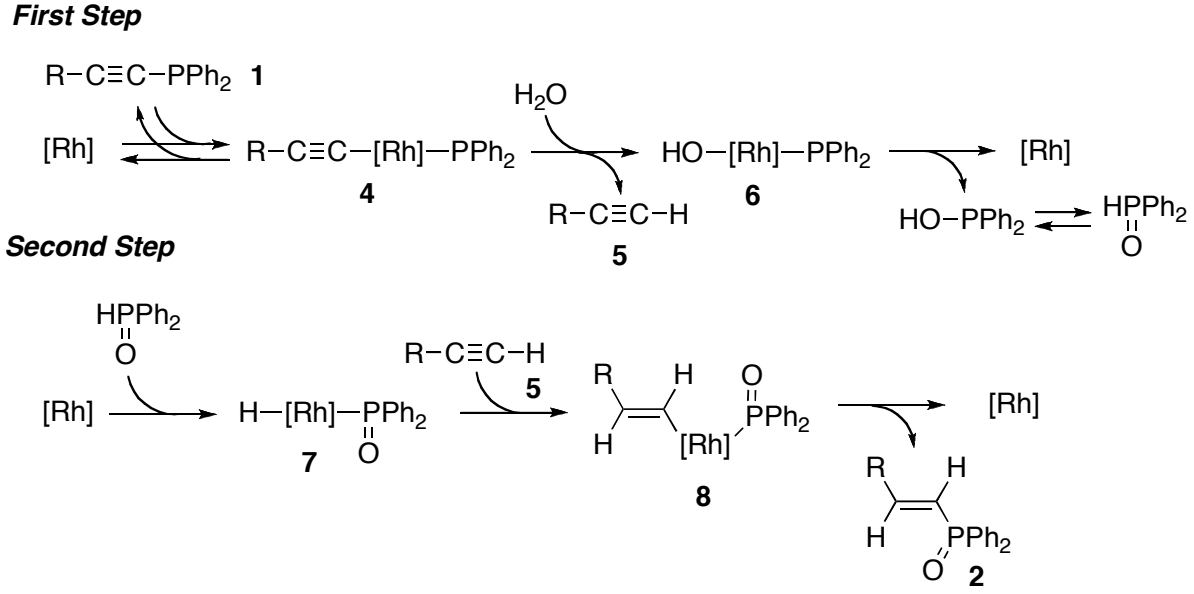
(1)



Based on these results, the author assumes that the reaction mechanism is as follows (Scheme 1). This reaction seems to consist of two steps. In the first step, C–P bond cleavage proceeds. Oxidative addition of 1-alkynylphosphine to a Rh(I) complex occurs to yield **4**. The oxidative addition would be reversible because no reacton took place in the absence of water (vide supra). Protonation with H_2O followed by reductive elimination provides 1-alkyne **5** and diphenylphosphine oxide. In the second step, rhodium-catalyzed hydrophosphinylation of 1-alkyne with diphenylphosphine oxide proceeds to yield 1-alkenylphosphine oxide. Oxidative addition of diphenylphosphine oxide occurs to afford **7**. Hydrorhodation of alkyne **5** followed by reductive elimination provides the product **2**. Such a rhodium-catalyzed hydrophosphinylation reaction has been reported.[3] Actually, treatment of 1-octyne with diphenylphophine oxide under the reaction conditions provided (*E*)-1-octenyldiphenylphosphine oxide in high yield (eq 3). This result supports the proposed mechanism. During the reaction, accumulation of neither diphenylphosphine oxide, 1-alkyne, nor rhodium hydride **7** was observed. Therefore, oxidative addition of diphenylphosphine oxide to a Rh(I) complex is not rate-determining step, since the use of D_2O retarded the reaction (eq 1).



Scheme 1. Plausible Reaction Mechanism



Conclusion

The author has found a reaction for the synthesis of (*E*)-1-alkenylphosphine oxides from 1-alkynylphosphines. The reaction is an interesting formal hydration reaction that involves carbon–phosphorus bond cleavage with a rhodium complex. Transition-metal-mediated carbon–phosphorus bond cleavage has been an attractive topic in organometallic chemistry.[4,5] The present reaction gives new information on the reactivity of 1-alkynylphosphine under rhodium catalysis.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to chloroform at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.0 ppm for ^{13}C. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. NMR yields were determined by fine ^{31}P NMR spectra with $(MeO)_3P{=}O$ as an internal standard. The first delay of ^{31}P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. For the preparation of **1**, chlorodiphenylphosphine was purchased from TCI. Starting 1-alkynylphosphines **1** were prepared by the methods described in Chapter 1. Chloro(bis-1,5-cyclooctadiene)rhodium(I) dimer was purchased from Wako Pure Chemicals. All reactions were carried out under argon atmosphere.

Typical Procedure for Rhodium-Catalyzed Reaction to Yield (*E*)-1-Alkenylphosphine Oxides

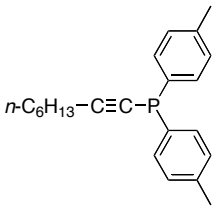
Synthesis of **2a** is representative. $[RhCl(cod)]_2$ (3.7 mg, 0.0075 mmol) was placed in a 20-mL reaction flask under argon. 1,4-Dioxane (3.0 mL), H_2O (0.30 mL), and 1-octynyldiphenylphosphine (**1a**, 0.15 g, 0.50 mmol) were sequentially added. The resulting solution was stirred for 3 h at reflux. After the mixture was cooled to room temperature, water (10 mL) was added, and the product was extracted with dichloromethane (10 mL × 3). The

combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded **2a** (0.11 g, 0.37 mmol, 73%) as a white solid.

Characterization Data

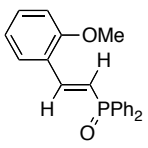
Phosphines **1a**,[6] **1b**,[6] **1c**,[7] **1d**,[8] **1e**,[9] **1f**,[10] **1g**,[7] **1h**,[11] and **1i**,[7] and phosphine oxides **2a**,[12] **2b**,[12] **2c**,[12] and **2f**[13] showed the same spectroscopic data as those described in the literature.

Bis(4-methylphenyl)-1-octynylphosphine (1j)



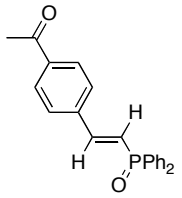
IR (neat) 3015, 2928, 2853, 2178, 1905, 1598, 1496, 1456, 1395, 1184, 1094, 1019, 803, 624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7.0 Hz, 3H), 1.27–1.37 (m, 4H), 1.46 (dd, *J* = 7.5, 7.5 Hz, 2H), 1.61 (dd, *J* = 7.5, 7.5 Hz, 2H), 2.33 (s, 6H), 2.43 (dt, *J* = 1.5, 7.5 Hz, 2H), 7.13–7.17 (m, 4H), 7.47–7.53 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.30, 20.64, 21.53, 22.81, 28.53, 28.55, 31.29, 76.23 (d, *J* = 1.6 Hz), 109.94 (d, *J* = 3.9 Hz), 129.24 (d, *J* = 7.6 Hz), 132.36 (d, *J* = 21.0 Hz), 133.84 (d, *J* = 4.9 Hz), 138.68; ^{31}P NMR ($CDCl_3$) δ –36.38. Found: C, 82.18; H, 8.62%. Calcd for $C_{22}H_{27}P$: C, 81.95; H, 8.44%.

(*E*)-1-Diphenylphosphinyl-2-(2-methoxyphenyl)ethene (2e)



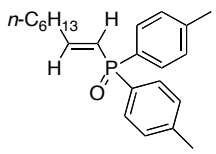
IR (nujol) 2923, 2853, 1598, 1484, 1461, 1247, 1181, 1004, 821, 744, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.94 (dd, *J* = 18.0, 24.0 Hz, 1H), 6.95 (dd, *J* = 8.5, 8.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 8.5 Hz, 1H), 7.44–7.55 (m, 7H), 7.73–7.83 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 55.41, 111.16, 119.69 (d, *J* = 104.1 Hz), 120.57, 124.12 (d, *J* = 17.1 Hz), 128.49 (d, *J* = 11.9 Hz), 128.76 (d, *J* = 1.0 Hz), 131.20, 131.43 (d, *J* = 10.0 Hz), 131.65 (d, *J* = 2.4 Hz), 133.35 (d, *J* = 104.5 Hz), 143.00 (d, *J* = 4.9 Hz), 158.08; ^{31}P NMR ($CDCl_3$) δ 23.09. Found: C, 75.11; H, 5.62%. Calcd for $C_{21}H_{19}O_2P$: C, 75.44; H, 5.73%. m.p.: 150.5–152.0 °C.

4-[(*E*)-2-(Diphenylphosphinyl)ethenyl]acetophenone (2g)



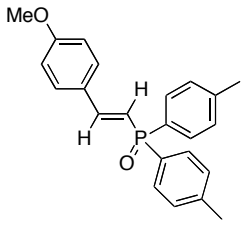
IR (nujol) 2924, 2853, 1678, 1603, 1438, 1359, 1270, 1182, 1107, 1000, 806, 746, 728, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.59 (s, 3H), 6.97 (dd, *J* = 17.5, 22.0 Hz, 1H), 7.44–7.57 (m, 7H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.70–7.79 (m, 4H), 7.95 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.63, 122.45 (d, *J* = 101.8 Hz), 127.83, 128.66 (d, *J* = 11.9 Hz), 128.79, 131.29 (d, *J* = 10.0 Hz), 132.01 (d, *J* = 2.5 Hz), 132.47 (d, *J* = 105.9 Hz), 137.80, 139.24 (d, *J* = 17.6 Hz), 145.93 (d, *J* = 3.4 Hz), 197.26; ^{31}P NMR ($CDCl_3$) δ 22.00. Found: C, 76.23; H, 5.54%. Calcd for $C_{22}H_{19}O_2P$: C, 76.29; H, 5.53%. m.p.: 176.0–177.5 ˚C.

(*E*)-1-Bis(4-methylphenyl)phosphinyl-1-octene (2j)



IR (neat) 2927, 2856, 1629, 1603, 1453, 1400, 1182, 1118, 1101, 807, 656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 7.0 Hz, 3H), 1.21–1.34 (m, 6H), 1.45 (tt, *J* = 7.0, 7.5 Hz, 2H), 2.26 (dt, *J* = 6.5, 7.5 Hz, 2H), 2.36 (s, 6H), 6.17 (dd, *J* = 17.0, 24.0 Hz, 1H), 6.66 (ddt, *J* = 17.0, 19.5, 6.5 Hz, 1H), 7.21–7.26 (m, 4H), 7.51–7.59 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.95, 21.48 (d, *J* = 1.0 Hz), 22.46, 27.80 (d, *J* = 1.0 Hz), 28.73, 31.47, 34.40 (d, *J* = 16.8 Hz), 122.00 (d, *J* = 102.6 Hz), 129.11 (d, *J* = 12.5 Hz), 130.05 (d, *J* = 106.4 Hz), 131.24 (d, *J* = 10.5 Hz), 141.92 (d, *J* = 2.9 Hz), 152.24 (d, *J* = 1.4 Hz); ^{31}P NMR ($CDCl_3$) δ 22.02. HRMS (EI^+) (*m/z*) Observed: 340.1954 (Δ = –0.7 ppm). Calcd for $C_{22}H_{29}OP$ [M^+]: 340.1956.

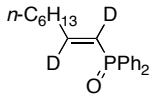
(*E*)-2-Bis(4-methylphenyl)phosphinyl-1-(4-methoxyphenyl)ethene (2k)



IR (nujol) 2924, 2855, 1602, 1511, 1464, 1438, 1378, 1307, 1257, 1176, 1100, 1020, 1002, 823, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 6H), 2.82 (s, 3H), 6.64 (dd, *J* = 17.5, 22.0 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.23–7.31 (m, 4H), 7.39 (dd, *J* = 17.5, 19.5 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.59–7.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.53 (d, *J* = 1.0 Hz), 55.31, 114.13, 116.78 (d, *J*

= 105.9 Hz), 128.06 (d, *J* = 18.1 Hz), 129.21 (d, *J* = 12.4 Hz), 129.14, 130.10 (d, *J* = 107.4 Hz), 131.36 (d, *J* = 10.5 Hz), 142.06 (d, *J* = 2.4 Hz), 146.51 (d, *J* = 3.8 Hz), 161.01; ^{31}P NMR ($CDCl_3$) δ 23.19. HRMS (EI$^+$) (*m/z*) Observed: 362.1433 (Δ = –0.8 ppm). Calcd for $C_{23}H_{23}O_2P$ [M$^+$]: 362.1436. m.p.:148.0–149.5 ˚C.

(*E*)-1,2-Dideuterio-1-diphenylphosphinyl-1-octene (2a–D)



IR (nujol) 2923, 2854, 1593, 1546, 1438, 1180, 1120, 722, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.20–1.36 (m, 6H), 1.46 (tt, *J* = 7.5, 7.5 Hz, 2H), 2.27 (dt, *J* = 2.0, 7.5 Hz, 2H), 7.40–7.53 (m, 6H), 7.64–7.71 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.48, 27.76, 28.74, 31.48, 34.27 (d, *J* = 16.3 Hz), 121.09 (dt, *J* = 101.3, 24.8 Hz), 128.42 (d, *J* = 12.0 Hz), 131.23 (d, *J* = 10.0 Hz), 131.58 (d, *J* = 2.9 Hz), 133.22 (d, *J* = 104.5 Hz), 152.46 (t, *J* = 23.4 Hz); ^{31}P NMR ($CDCl_3$) δ 21.78. ^{2}H NMR ($CDCl_3$) δ 6.20, 6.73. HRMS (EI$^+$) (*m/z*) Observed: 314.1767 (Δ = –0.4 ppm). Calcd for $C_{20}H_{23}D_2OP$ [M$^+$]: 314.1769. m.p.:58.0–60.0 ˚C.

References and Notes

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(2) The *tert*-butyl group would retard the oxidative addition (Scheme 1). Treatment of *tert*-butylacetylene with diphenylphosphine oxide under conditions similar to those in eq 3 led to smooth hydrophosphinylation.

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Publication List

I. Parts of the present thesis have been published in the following journals.

General Introduction

1-Alkynylphosphines and Their Derivatives as Key Starting Materials in Creating New Phosphines

Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Chem. Asian J. in press

Chapter 1 Copper-Catalyzed *anti*-Hydrophosphination Reaction of 1-Alkynylphosphines with Diphenylphosphine Providing (*Z*)-1,2-Diphosphino-1-alkenes

Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

J. Am. Chem. Soc. **2007**, *129*, 4099–4104.

Chapter 2 Palladium-Catalyzed *anti*-Hydrothiolation of 1-Alkynylphosphines

Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Org. Lett. **2007**, *9*, 1383–1385.

Chapter 3 Regio- and Stereoselective Hydroamidation of 1-Alkynylphosphine Sulfides Catalyzed by Cesium Base

Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Org. Lett. **2008**, *10*, 3093–3095.

Chapter 4 Synthesis of Bulky Phosphines by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides

Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

J. Am. Chem. Soc. **2007**, *129*, 6996–6997.

Chapter 5 New Synthesis of 2-Indolylphosphines by Palladium-Catalyzed Annulation of 1-Alkynylphosphine Sulfides with 2-Iodoanilines

Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

To be submitted.

Chapter 6 Rhodium-Catalyzed Reaction of 1-Alkynylphosphines with Water Yielding (*E*)-1-Alkenylphosphine Oxides

Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Bull. Chem. Soc. Jpn. **2008**, *81*, 502–505.

II. Other Publications not included in this thesis.

(1) Stereoselective Hydrothiolation of Alkynes Catalyzed by Cesium Base: Facile Access to (*Z*)-1-Alkenyl Sulfides

Azusa Kondoh, Kazuaki Takami, Hideki Yorimitsu, and Koichiro Oshima

J. Org. Chem. **2005**, *70*, 6468–6473.

(2) Nucleophilic Aromatic Substitution Reaction of Nitroarenes with Alkyl- or Arylthio Groups in Dimethyl Sulfoxide by Means of Cesium Carbonate

Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Tetrahedron **2006**, *62*, 2357–2360.

(3) A New Approach to 4-Aryl-1,3-butanediols by Cobalt-Catalyzed Sequential Radical Cyclization-Arylation Reaction of Silicon-Tethered 6-Iodo-1-hexene Derivatives

Hidenori Someya, Azusa Kondoh, Akinori Sato, Hirohisa Ohmiya, Hideki Yorimitsu, and Koichiro Oshima

Synlett **2006**, 3061–3064.

(4) Carbocupration of 1-Alkynylphosphines Followed by Trapping with Electrophiles

Shigenari Kanemura, Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Org. Lett. **2007**, *9*, 2031–2033.

(5) Intermolecular Radical Addition of Alkylthio- and Arylthiodiphenylphosphines to Terminal Alkynes

Tatsuya Wada, Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Org. Lett. **2008**, *10*, 1155–1157.

(6) Regio- and Stereoselective Additions of Diphenyldithiophosphinic Acid to *N*-(1-Alkynyl)amides and 1-Alkynyl Sulfides

Shigenari Kanemura, Azusa Kondoh, Hiroto Yasui, Hideki Yorimitsu, and Koichiro Oshima

Bull. Chem. Soc. Jpn. **2008**, *81*, 506–514.

(7) Synthesis of Bulky Arylphosphanes by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reaction and Their Use as Ligands

Takayuki Kobatake, Azusa Kondoh, Suguru Yoshida, Hideki Yorimitsu, and Koichiro Oshima

Chem. Asian J. **2008**, *3*, 1613–1619.

(8) Nickel-Catalyzed Cross-Coupling Reactions of Alkyl Aryl Sulfides and Alkenyl Alkyl Sulfides with Alkyl Grignard Reagents Using (*Z*)-3,3-Dimethyl-1,2-bis(diphenylphosphino)-but-1-ene as Ligand

Shigenari Kanemura, Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Synthesis **2008**, 2659–2664.

(9) Radical Addition of Polyhaloalkanes to 2-Ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Tatsuya Wada, Yuto Sumida, Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Bull. Chem. Soc. Jpn. **2009**, *82*, 1433–1435.

(10) Rhodium-Catalyzed Dehydrogenative Borylation of Cyclic Alkenes

Azusa Kondoh and Timothy F. Jamison

Chem. Commun. in press

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Azusa Kondoh